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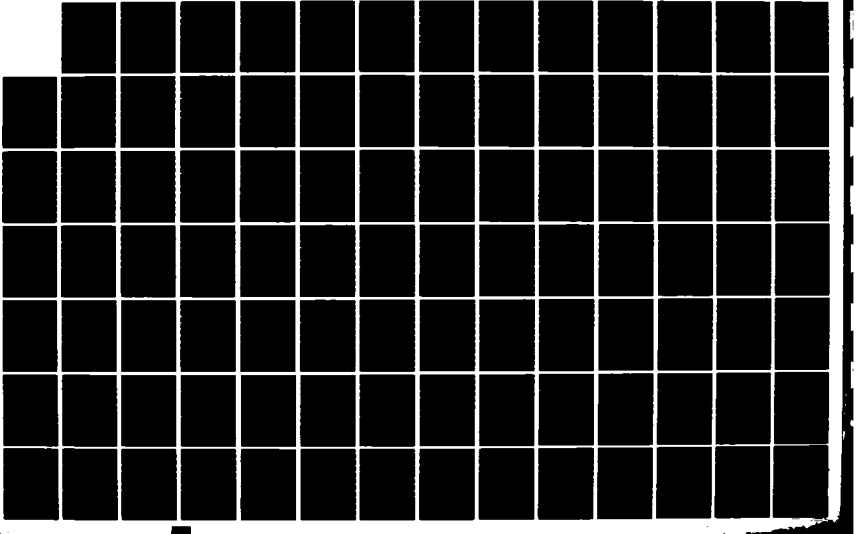

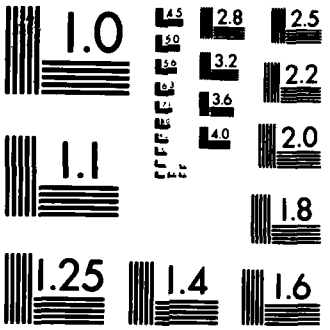

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Book of Abstracts

1983 IEEE International Symposium on

APPLICATIONS OF FERROELECTRICS (ISAF)

June 1-3, 1983

National Bureau of Standards
Gaithersburg, Maryland

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ABSTRACTS

1983 IEEE INTERNATIONAL SYMPOSIUM ON

APPLICATIONS OF FERROELECTRICS (ISAF)

JUNE 1 - 3, 1983

NATIONAL BUREAU OF STANDARDS
GAITHERSBURG, MARYLAND

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AMERICAN CERAMIC SOCIETY
(ELECTRONICS DIVISION)

Wednesday, June 1

8:15 a.m.	Registration, NBS
9:00	Opening Remarks - R. C. Pohanka, Office of Naval Research,USA
	Welcome - R. Mehrabian, National Bureau of Standards, USA
9:15	Keynote Speaker - W. Heywang, Siemens, Federal Republic of Germany

Partial Contents:

9:45 SESSION 1A: Electro-Optics
Chairman: C. Land

1A-1 Ferroelectric Displays: Past, Present, Future; (invited) - G. W. Taylor, Princeton Resources, USA

1A-2 Ferroelectrics in Phase-Conjugate Optics and Dynamic Holography; (invited) - P. Gunter, ETH-Zurich, Switzerland

Cont'd Pg V

Ferroelectric Displays: Past, Present, Future (invited) - G.W. Taylor, Princeton Resources, USA

(No Abstract)

Ferroelectrics in phase-conjugate optics and dynamic holography

P. Günter
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Swiss Federal Institute of Technology
ETH Hoenggerberg
CH-8093 Zürich, Switzerland

In recent years ferroelectric materials with their large electro-optic coefficients have found new optical applications in the field of phase conjugate optics, image processing and dynamic holography. These applications are based on the photoinduced refractive index changes or photorefractive effect which is due to the linear electro-optic effect driven by photoinduced space-charge fields.

Mixing two coherent optical beams in the volume of a photorefractive material leads to a refractive index grating which can be phase shifted with respect to the interference pattern produced by the two waves. Such a volume hologram recording can give rise to a considerable energy transfer between the two beams diffracted by the own grating. This beam coupling effect via the recorded hologram can be useful for coherent light amplification of time variing light beams. Since the grating shift depends on the recording mechanism, measurements of the energy transfer can also give additional information on the nature of the photorefractive effects. On the other hand with a detailed knowledge of the photorefractive recording mechanism it is possible to optimize the grating phase shift with a suitable choice of physical parameters (applied electric field, fringe spacing, recording wavelength etc.) and to control the gain in energy transfer experiments with these parameters.

Our experiments show, that with a proper choice of experimental parameters, light beams can be coherently amplified by two-wave mixing in reduced $KNbO_3$ crystals, with a maximum steady-state exponential gain of $g = 10\ cm^{-1}$.

Interesting applications in real-time processing, focussing and restoration of optical wave-fronts have been proposed by four-wave mixing in electro-optic materials under the condition of spatial synchronism between interacting beams. Complex conjugate waves can be generated and weak beams can be simultaneously enhanced.

The experiments show, that photoconductive ferroelectrics with large electro-optic coefficients (e.g. $KNbO_3:Fe^{2+}$, $BaTiO_3$, $Ba_2NaNb_5O_{15}$, $Ba_{1-x}Sr_xNb_2O_6$) are extremely interesting for applications in the field of optical phase conjugation, in "real-time" holography and optical image amplification.

The relevant materials parameters of ferroelectrics for these applications will be discussed and compared with the data found in non-ferroelectrics. A few applications of optical phase conjugation using ferroelectric crystals will also be discussed.

9:45 SESSION 1B: Piezoelectrics
Chairman: W.N. Lawless

1B-1 Ferroelectric Composites (invited) - R. E. Newnham, The Pennsylvania State University, USA

1B-2 Biomedical Applications of Piezoelectric and Pyroelectric Polymers (invited) - D. DeRossi, University of Pisa, Italy

10:45 Coffee

Cont'd Pg. viii

Ferroelectric Composites (invited) R. E. Newnham, The Pennsylvania State University U.S.A.

(no abstract)

Biomedical Applications of Piezoelectric and Pyroelectric Polymers (invited)
D. DeRossi, University of Pisa, Italy

(no abstract)

11:15 a.m. SESSION 2A: Dielectrics (Aging)
Chairman: K. Richie

2A-1 Ceramics for Microwave Dielectric Resonator (invited) - S. Nomura, Tokyo Institute of Technology, Japan

2A-2 The Effects of Composition and Microstructure on Electrical Degradation in $BaTiO_3$ - M. P. Harmer, Y. H. Hu, M. Lal and D.M. Smyth, Lehigh University, USA

2A-3 Study of the Relaxation of the Permittivity in Doped and Gamma-Irradiated TGS Single Crystals - W. Windsch, L. Gawrisch and H. Schlemmbach, Karl Marx Universität, German Democratic Republic

2A-4 Aging Changes in Electrical and Mechanical Properties of $Pb(Zr, Ti)O_3$ Family Ceramics - K. Okazaki, National Defense Academy, Japan

2A-5 Polarization Reversal in CsH_2PO_4 - S. Fujimoto, N. Yasuda and S. Asahi, Gifu University, Japan

2A-6 Microscopic Observations of Electric Field Effect on the Nucleation of Domains Near a Ferroelectric Transition - N. S. Dalal, West Virginia University, USA

2A-7 The Mechanism of Remnant Birefringence and the Surface Structure of Transparent Ferroelectric Ceramics - A.E. Krumins, A.E. Kapenieks, L.A. Shebanov and V.I. Dimza, Latvian State University, USSR

Ceramics for Microwave Dielectric Resonator

S.NOMURA, K.TOYAMA and K.KANETA

Department of Physical Electronics, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152

This paper reviews our investigations on ceramics with temperature-stable high dielectric constant and low microwave loss suited for dielectric resonator. The ceramics involved in our study are $A(B_{1/3}B'_{2/3})O_3$(A: Ba, Sr, B: Mg, Zn, B': Nb, Ta) perovskite oxides as well as $Ba_2Ti_9O_{20}$ and $Zr_{0.8}Sn_{0.2}TiO_4$. We prepared the ceramic samples with minute addition of Mn (1~2 mol %) to complete the sintering and decrease the dielectric loss at microwave frequnecy. The sintering was made at 1500~1600°C for the perovskites and at 1400°C for $Ba_2Ti_9O_{20}$ and $Zr_{0.8}Sn_{0.2}TiO_4$. The values of relative dielectric constant of the well sintered ceramics with the Mn addition are , for example, 25 ($Ba(Mg_{1/3}Ta_{2/3})O_3$), 30($Ba(Zn_{1/3}Ta_{2/3})O_3$), 33 ($Ba(Mg_{1/3}Nb_{2/3})O_3$), 38($Sr(Zn_{1/3}Nb_{2/3})O_3$) and 40 ($Ba(Zn_{1/3}Nb_{2/3})O_3$) ; the unloaded Q values at 10 GHz are 17000, 16000, 6000, 3700 and 5400 respectively. A small temperature coefficient of the resonant frequency less than ± 10 ppm/°C can be realized by making appropriate solid solutions between the perovskite compounds.

An improvement in the Q value due to the Mn addition was shown also in $Ba_2Ti_9O_{20}$ and $Zr_{0.8}Sn_{0.2}TiO_4$; the Q value more than 5000 was obtained at 10 GHz. In all the cases, the Q value was quite sensitive to the annealing condition at high temperature. The origin of the dielectric loss at microwave frequency will be discussed, relating to the effect of Mn addition. Some of dielectric application will be given.

The Effects of Composition and Microstructure on Electrical Degradation in $BaTiO_3$

M. P. Harmer, Y. H. Hu, M. Lal, and D. M. Smyth
Materials Research Center
Lehigh University
Bethlehem, PA 18015

When subjected to electrical fields in the KV/cm range at 100°C and above, $BaTiO_3$ ultimately undergoes gradual degradation in the form of steadily increasing current. This has been generally attributed to the migration of oxygen vacancies with resulting distortion of the field distribution. Degradation rates have been measured for $BaTiO_3$ samples having different Ba/Ti ratios and additions of acceptor and donor impurities. The measurements have been made as a function of composition at constant grain size and as a function of grain size at constant compositions. The effects of BaO-rich and TiO_2-rich second phases have been investigated. The results will be correlated with the known defect chemistry of $BaTiO_3$. (Supported by the Office of Naval Research.)

Study of the relaxation of the permittivity in doped and gamma-irradiated TGS single crystals

W. Windsch, L. Gawrisch, H. Schlemmbach
DDR, Karl-Marx-Universität, Sektion Physik,
7010 Leipzig, Linnéstraße 5

The knowledge of the mechanism of the stabilization of the spontaneous polarization in ferroelectric crystals due to lattice defects is important for the development of materials for pyroelectric detectors and other devices.

The change of the permittivity in gamma-irradiated and Cr^{3+}- and VO^{2+}-doped TGS single crystals after switching of an applied d.c. electric field in dependence on electric field strenght and temperature is investigated. Two types of the relaxational behaviour of the permittivity in dependence on the direction of the applied d.c. field relative to the internal bias field was observed. For relaxation type 1 the permittivity increases in a time shorter than 1 sec to a maximum value and then it decreases monotonously to the equilibrium value ε_∞. The relaxation type 2 shows firstly a decrease to a minimum followed by an increase to ε_∞.

Domain structure investigations show that both types of relaxational behaviour are observed in TGS crystals with different domain volumes for both directions of the spontaneous polarization (unipolar crystals). Type 1 is observed if the major component of the domain volume which consists of large domains is decreased by means of the external electric d.c. field, type 2 for decreasing of the minor component which consists of very much small domains.

The relaxation processes can be described in a good approximation by superposition of three exponentials with relaxation times τ_i between 10^4 sec and 1 sec.

Since the piezoelectric effect and the effect of space charges on the permittivity are here negligibly small the measured change of the permittivity corresponds essentially to the change of the domain wall area during the switching and the relaxation towards the equilibrium state. The influence of the lattice defects on the relaxational perameters can by clearly shown.

Aging Changes in Electrical and Mechanical Properties of $Pb(Zr,Ti)O_3$ Family Ceramics

Kiyoshi Okazaki
The National Defense Academy, Hashirimizu, Yokosuka 239, Japan

Abstract

In 1959, Okazaki investigated the aging effects in $BaTiO_3$ ceramics, and found a loop-shape change in D-E loops from "normal" at just after the thermally depolarization above the Curie point to "propeller"(anti-ferroelectric like) during the aging process at below the Curie point. Also it was found that "almost normal" loop just after the poling by applying a dc field was gradually changed into "asymmetric" loop with the aging time at below the Curie point. These phenomena can be explained by an "internal bias field" (hereinafter E_i) inside every ferroelectric domains generated during the aging process. Several researchers have also investigated the loop-shape changes in $Pb(Zr,Ti)O_3$ ceramics and found the same E_i.

In the hot-pressed $Pb_{1-1.5\cdot x}La_xTiO_3$ [x=0.15] with a tetragonality of c/a=1.028, the internal stress was measured using a micro-indentation technique with various loads of indent. It is noticed that the internal stress is gradually decreased with the aging time from the thermally depolarized state. This suggests that the aging change of internal stress is one of the stress-releasing process with the domain rearrangements.

In this paper, the aging changes in electrical and mechanical properties of $Pb(Ti,Zr)O_3$ family ceramics will be reviewed with the related experimental results and the origins of E_i will be discussed with the importance of sample-history such as aging time, dc and/or ac applications etc in property-measurements of ferroelectric ceramics.

Polarization Reversal in CsH_2PO_4

Sanji Fujimoto, Naohiko Yasuda and Shigeo Asahi
Department of Electrical Engineering, Gifu University, Yanagido, Gifu, Japan

We have presented dielectric properties of CsH_2PO_4(CDP) and indicated that the three dimensional correlation of polarizations among the chains of the hydrogen bond along the b-axis is very weak due to the one dimensional nature of CDP[1]. Here we present the switching behaviour in CDP. The bell-shaped switching current transient can be observed along the ferroelectric b-axis below the Curie point T_c=-120°C at atmospheric pressure, and its shape is characterized by the maximum switching current i_{max}, the switching time t_s and the symmetry m=t'/t", where t' is the rise time and t"=t_s-t' is the decay time. The field E dependence of i_{max} or t_s^{-1} is expressed by the following relations; i_{max} or $t_s^{-1} \propto (E-E')$, E' is a constant, for the high field region, and i_{max} or $t_s^{-1} \propto \exp(-\alpha/E)$, where α is the activation field, for the low field region. The temperature T dependence of the mobility μ of the domain wall motion is expressed by the relation $\mu \propto \exp(-W/kT)$, where W is the activation energy for the domain wall motion and k is the Boltzmann's constant, and W≒0.05eV at atmospheric pressure. The activation field α increases with decreasing T. The symmetry m increases and saturates with increasing E(m≒0.8). Namely the shape of the switching transient becomes more symmetrical with E. Since t_s is short at very low temperatures(e.g. t_s=40μsec at 1kV/cm at -180°C), CDP might be used as switching and memory devices in the cryogenic field.

1. N.Yasuda, S.Fujimoto et al, Phys.Rev.B20 2755 (1979)

MICROSCOPIC OBSERVATIONS OF ELECTRIC FIELD EFFECT ON THE NUCLEATION OF DOMAINS NEAR A FERROELECTRIC TRANSITION

N. S. Dalal
Department of Chemistry, West Virginia University, Morgantown, WV 26506

Using structure-specific "spin" probes, we have developed an electron paramagnetic resonance (EPR) technique for observing, at molecular level, the process of nucleation of domains in the vicinity of a ferroelectric phase transition. The method can be used for studying the effect of externally applied electric field strength (E) on the growth of a domain with a given polarity, and the temperature dependence of the rate of domain growth or switching as a function of E. These data obtained around T_c are thought to provide perhaps the first experimental verification of recently proposed theoretical model of a order-disorder phase transition in ferroelectric crystals. This presentation will focus on details of the experimental technique and its applications to domain switching in the KH_2PO_4-type of ferroelectrics.

THE MECHANISM OF REMNANT BIREFRINGENCE AND THE SURFACE STRUCTURE OF TRANSPARENT FERROELECTRIC CERAMICS

A.E.Krumins, A.E.Kapenieks, L.A.Shebanov, V.I.Dimza

Institute of Solid State Physics, Latvian State University, 226063 Riga, USSR

Some remnant birefringence (RB) is observed in transparent ferroelectric ceramics PLZT-10 after extended exposure to the applied field, this being responsible for a decrease of contrast in devices made on the basis of the material /1/.

The RB is shown to grow with the amplitude and duration of the controlling field and to decrease with the growth of temperature. A study of the RB distribution in the gap between planar electrodes shows that an essential part of the RB is localized near the electrodes, the distribution being asymmetric - the RB is much larger near the cathode as compared to the anode. The surface conditions strongly determine the RB.

The analysis of experimental results suggests that the RB is due to the space charge. The latter accumulates in the region adjacent to the electrodes as a result of the carrier injection therefrom.

The polished surface of PLZT-10 ceramics has been studied by X-ray and photoelectric methods. The X-ray data have shown appearance of two layers after the surface polishing: the amorphous outer layer 100 nm thick and 1000 nm thick defected inner layer of a structure different from that of the bulk. The inner layer has a different (as compared to the initial state) concentration of vacancies in Pb and Ti sublattices. The effects of preliminary annealing and chemical etching on the surface structure, photoelectric and other properties of the transparent ferroelectric ceramics have been studied.

The data on surface structure of the PLZT ceramics are used to explain the experimental results of carrier transfer from the metallic point electrodes to the surface levels of the ferroelectric ceramics /2/ and to reveal some particular features of the remnant birefringence mechanism.

1. G.Wolfram, Ferroelectrics, 1976, vol.27, pp.173-177.
2. A.E.Krumins, U.J.Ilyin, V.I.Dimza. J.of Technical Physics (in Russian), vol.52, 1982, pp.2107-2108.

11:15 a.m. SESSION 2B: Piezoelectrics (Devices)
Chairman: R. Ting

2B-1 Hydro-Piezoelectric Power Generation from Ocean Waves - G. W. Taylor and J. R. Burns, Princeton Resources, USA

2B-2 Multi-Focus Ultrasonic Transducer - H. P. Beerman, Analogic Corporation, USA

2B-3 A New Approach to the Gravitational-Waves Detection by Employing Elastic Plates and Piezoelectric Cells- L. Novakovic, The Svetozar Markovic University, Yugoslavia

2B-4 A New Type of the Piezoceramic Wave Filter for the Frequency Range 200-500 kHz - J. Zelenka, College of Mechanical and Textile Engineering, Czechoslovakia

2B-5 Consequential Quality Control in Manufacture of High Reliability Piezoceramic Transducer - M. Passaris and Z. Jandera, Plessey, Australia

2B-6 Dome Shaped Piezopolymer Transducers- F. Micheron and P. Ravinet, Thomson-CSF, France

2B-7 Frequency Response and Acoustic Behavior of Polyvinylidene Fluoride - D.K. Das-Gupta and K. Doughty, University College at North Wales, UK; R. J. Shuford and Y. Hinton, Army Materials and Mechanics Research Center, USA

HYDRO-PIEZOELECTRIC POWER GENERATION FROM OCEAN WAVES

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A new concept is proposed for the large scale generation of electrical power from deep water, ocean waves. The concept is based on using large areas of multi-layered piezoelectric polymers to directly convert, on a continuous basis, the essentially unlimited mechanical energy present in the ocean waves into high voltage, low frequency electrical energy.

The concept termed Hydro-piezoelectric Power Generation, would appear to have many intrinsic advantages as a primary energy source. The piezoelectric plastic and the structure for supporting it and its installation below the ocean surface is inherently low cost. Wave powers in the range 10 to 80 kW/meter are available on a continuous 24 hour a day, 365 day a year basis. There are no moving parts to wear out and the polymer is resistant to corrosion. The high voltage output permits low loss transmission.

Based on some preliminary experimental results on the polymer PVF_2 and making some conservative assumptions, including some anticipated improvements, it has been calculated that a 100 MW hydro-piezoelectric power station would have a plant cost of $1.25 per watt and could deliver power to an onshore grid at a cost of 2.5 cents per KWH. These numbers are very attractive compared to existing and other proposed primary energy sources.

MULTI-FOCUS ULTRASONIC TRANSDUCER

Henry P. Beerman

Analogic Corporation

Wakefield, MA 01880

A B S T R A C T

An ultrasonic transducer is described that, within a single unitary structure, has a plurality of different focal lengths. The transducer consists of a piezoelectric element having a cylindrical spiral-shaped surface, with respective zones of the spiral surface providing different focal lengths. The piezoelectric element is a plastic piezoelectric film of polyvinyledene fluoride (PVF_2) or a sandwich of PVF_2 and PZT. For receiving only, PVF_2 suffices; while for additional transmitting, a PVF_2/PZT sandwich is required.

The individual curved zones provide focussing in one dimension and all the foci lie in a plane located transversely to the spiral surface. To obtain additional focussing in the orthogonal dimension, a Fresnel zone electrode pattern is deposited on the front surface of each section of the piezoelectric film and extends across the width of the film. The Fresnel zone pattern for each section is slightly different than the others to account for the different focal lengths. A common electrode is provided on the rear surface of the PVF_2 film. The piezoelectric film or composite is supported on a backing of acoustic damping material.

The transducer could find application as an immersion transducer for medical diagnostic purposes or for SONAR, in which case the transducer dimensions must be scaled up to accommodate the lower frequencies of SONAR.

The multi-focus ultrasonic transducer represents a concept on which a patent is pending.

A NEW APPROACH TO THE GRAVITATIONAL-WAVES DETECTION BY EMPLOYING ELASTIC PLATES AND PIEZOELECTRIC CELLS

by
Ljubisav Novaković

Physics Department, The Svetozar Marković University, 34000 Kragujevac
Yugoslavia

There is a growing conviction that gravitational waves, coming from distant cosmic objects, will be discovered and analyzed under the terrestrial laboratory conditions. It is the purpose of the present work to expose a physical basis for using very sensitive piezoelectric cells on a mechanical Earth-fixed detector to materialize a direct coupling of gravity waves, or the space-time curvature, with piezoelectricity, where a resonant bar is replaced by a number of thin two-dimensional elastic plates. Actually we suggest a quadratic shape for the plates with approximate dimensions 2m x 2m x 10^{-3} cm. We also suggest that every thin two-dimensional elastic plate should be firmly and uniformly clamped all over its quadratic circumference on a solid frame. We assume that such a clamping will suppress both degrees of freedom of the vibrational motion in the plane of the plate, but will disclose the vibrational degree of freedom along the direction which is perpendicular to the plane of the plate.

This device, as part of the experimental apparatus, will ensure the action of only two important forces, one coming from the gravitational wave, and another induced by an elastic strength along the direction which is normal to the plate. We have all physical reasons to conclude that piezoelectric cells, every one fixed at the centre of each thin two-dimensional elastic plate, will manifest an immediate presence of the gravitational wave coming from the vertical direction and falling on a reliable test body. (For this reason we propose that four identical thin elastic plates should be constructed around a long solid rope, the top end of the rope being fixed at the ceiling of a vacuous chamber, so the entire apparatus will then look like a huge chandelier.)

The problem of identifying and measuring the frequencies which correspond to stable stationary modes could be solved by assuming that piezoelectric cells, each having a negligible mass compared to the elastic plates, must be attached to the middle points on the plates in such a way that they both possess identical relevant physically characteristic properties, in particular, the eigenfrequencies and resistive coefficients.

A NEW TYPE OF THE PIEZOCERAMIC WAVE FILTER FOR THE FREQUENCY RANGE 200 - 500 kHz

JIŘÍ ZELENKA

College of Mechanical and Textile Engineering
Liberec, Czechoslovakia

The PZT type of the ferroelectric ceramics is used for the construction of the new monolithic filter. The design of the filter goes out of the phenomenon of the energy trapping of width-extensional vibrations in the thin piezoelectric strips what was first observed by Watanabe, Nakamura and Shimizu and described in the paper Ref. 1. The ide a of the filter was briefly given in the paper Ref. 2.

The filter is composed of one or two thin narow bars on which two or three elastically coupled resonators are placed while the electric coupling is applied between the bars. The extreme bandwidth of the filter is about 2.5 % of the nominal frequency and the input and output impedances are from 1 to 2 kOhm at the frequency 450 kHz. The information about the design and the results of the measurement of the filter is given in the paper.

REFERENCES

1. H. Watanabe, K. Nakamura and H shimizu. IEEE Trans. Son. Ultrason. SU-18, 265 (1981).

2. J. Zelenka. Proc. SSCT, Prague July 12 - 16, 1982, pp 463 - 467.

CONSEQUENTIAL QUALITY CONTROL IN MANUFACTURE OF HIGH RELIABILITY PIEZOCERAMIC TRANSDUCER.

M. Passaris, Z. Jandera.

Plessey, Australia

ABSTRACT

Plessey Australia were awarded a contract to supply transducers to Honeywell for the Mulloka Project. The vibrator final capacitance specification is ± five %.

This tight tolerance and technological requirements posed a problem to the business as the existing company quality system were not considered suitable for application into this product.

As a result a product assurance programme was designed to complement the requirements of the transducer specification and subsequent manufacturing processes.

The elements of this programme include :

Design evaluation.
Raw material evaluation.
Sub-contractor control.
Procured material control.
Process and quality control.
Test and inspection.
Product release.

DOME SHAPED PIEZOPOLYMER TRANSDUCERS

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THOMSON CSF - LCR
B.P. 10 - 91401 - ORSAY - France

ABSTRACT

Recent processes in our processing technology of piezopolymer films such as PVF_2 have made possible to extend their thicknesses in the range of the millimiter ; such available thicknesses enlarge their domain of applications, specially in the field of the new electroacoustic transducers which are presented there. The basic configuration of these transducers is the thick dome shaped shell which static and dynamical mechanichal behaviour is reported first ; both extensional and flexural effects are taken into account, which allows to compute their acoustic mass and compliance and the frequency of their first resonance mode. The limiting case of the dome shaped membrane is deduced from this analysis.

A general formulation of the microphone sensitivity and transmitter (earphones and loudspeakers) efficiency is reported, in terms of the different geometrical and material parameters. Three detailed applications are considered : a telephone microphone, using a thick monolithic PVF_2 diaphragm, a telephone receiver using a laminated (stacked films electrically in parallel) PVF_2 membrane, and a tweeter using a thin PVF_2 membrane. Comparisons between computed and measured characteristics are discussed, with a special attention to the storage and operating temperature stability of the microphone.

Frequency Response and Acoustic Behaviour of Polyvinylidene fluoride

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G.B.

and

R. J. Shuford and Y. Hinton,
Department of the Army,
Army Materials and Mechanic Research
Centre,
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Abstract

The piezo- and pyroelectric response of suitably poled polyvinylidene fluoride (PVF_2) films are significantly greater than those of other polymers. The mechanical strength of the PVF_2 film, together with its flexibility and reasonably uniform piezoelectric response over a wide frequency bandwidth makes it a useful sensing material for transducer devices of diverse applications, viz., detection of acoustic emission originating from (i) deformation in materials under mechanical stress and (ii) partial discharges and 'tree growth' prior to electrical breakdown in dielectrics under electrical stress.

It is established that a value of 20×10^{-12} CN^{-1} may be obtained with stretched (5:1 stretch ratio) and corona poled (4×10^{8} Vm^{-1}) PVF_2 films. However, it should be emphasized that the frequency response of d_{31} is of primary importance in the fabrication of a piezoelectric transducer with a wide bandwidth. Furthermore, the frequency dependence of the acoustic loss factor, Q, and the electromechanical coupling factor, K^2, which determine the equivalent circuit impedance, are also of interest for high frequency ultrasonic applications.

Present work reports an investigation of the electro-acoustic properties of corona poled PVF_2 film of thickness 25 μm over a range of frequencies from 10 Hz to 1 MHz at ambient temperature. Furthermore, the piezoelectric response of an experimental broadband transducer using PVF_2 film as the sensing element is also provided.

2:00 p.m. SESSION 3A: Electro-Optics-1
Chairman: F. Micheron

3A-1 Applications of Ferroelectrics in Optical Information Processing (invited) - C. Warde, Massachusetts Institute of Technology, USA

3A-2 Microstructure and Properties of Some Electro-Optic Ceramics (invited) - K. Okazaki, National Defense Academy, Japan

3A-3 New Transparent Ceramics for Electro-Optic Applications - A. Gutu-Nelle, H. Schichl and J. Springer, Standard Elektrik Lorenz, Federal Republic of Germany

3A-4 Specific Features of Holographic Recording in Transparent Ferroelectric Ceramics - A. E. Krumins and J. A. Seglins, Latvian State University, USSR

3A-5 Nonhomogeneity of Phase Modulation by PLZT Retardation Plate - M. Ozolinsh, A. Kapenieks and A. Krumins, Latvian State University, USSR

Applications of Ferroelectrics in Optical Information Processing (Invited)

C. Warde, Massachusetts Institute of Technology, U.S.A.

(no abstract)

Microstructure and Properties of Some Electrooptic Ceramics

Kiyoshi Okazaki

The National Defense Academy, Yokosuka 239, Japan

In this paper, recent developed electrooptic ceramics with tungsten-bronze structure, mechanical properies of PLZT ceramics using a micro-indentation technique, properties of some transparent ceramics prepared from fine raw powders and anisotropies originated from the grain oriented behaviors will be reviewed.

In the tungsten-bronze typed materials, the hot-pressed $(Sr,Ba)Nb_2O_6$ [SBN] ceramics showed a transmittance of 42-52% in a wave length of 0.35 to 1.4 μm. Also in the hot-pressed $(Pb_xBa_{1-x})_{1-3y/2}La_yNb_2O_6$ [PBLN] ceramics, the linear and quadratic electrooptic coefficients were 3.04×10^{-10} m/V for x/y=70/2 and 2.78×10^{-16} m^2/V^2 for 60/8, respectively.

For the evaluation of mechanical behaviors of ferroelectric ceramics, the micro-indentation technique was applied to the hot-pressed pore-free PLZT ceramics with tetragonal, rhombohedral and cubic structures at room temperature, respectively, and the effective fracture toughness, the internal stress generated during the para- to ferroelectric phase transition and the aging changes of internal stress were measured and discussed.

Using raw fine powders with a particle size of 0.1 μm of Ti and/or Zr compounds, PLZT ceramic samples were hot-pressed and the dielectric, piezoelectric and electrooptic properties were measured and discussed on the special processing, the microstructure and the homogeneities compared to the normal PLZT using the metal oxide raw powders.

In the hot-pressed tungsten-bronze or bismuth layer structured ceramics, we found some anisotropic electrooptic properties related to the grain orientations of elongated grains or plate-like grains.

NEW TRANSPARENT CERAMICS FOR ELECTRO-OPTIC APPLICATIONS

A. Gutu-Nelle, H. Schichl and J. Springer

Standard Elektrik Lorenz, Federal Republic of Germany

Extremely high electro-optical constants and relatively low permittivity have been reported from earth-alkali niobate single-crystals with tungsten bronze structure. Transparent ceramics produced of these compounds promised to be an interesting alternative to lanthana doped perowskites known as PLZT and used for electro-optic modulators and light-gates. The disadvantages of the PLZT are high switching voltage and high permittivity which limit switching time to 10 µs due to the large currents required for switching. Starting from the compound $Ba_6Ti_8Nb_8O_{30}$ a ceramic material was developed which is a good candidate for use in electro-optical applications. Transparency and optical isotropy could be achieved by replacing about 10 % of the BaO by La_2O_3 and by the use of a coprecipitation method for powder preparation and a vacuum sintering process for ceramic fabrication. The transparency of the so prepared ceramics is similar to that of PLZT, the range of light transmission lies between 350 nm and 6000 nm. The room temperature permittivity of the material is only a seventh of that of PLZT so allowing a switching frequency which is also higher by the same factor. The contrast ratio at a switching voltage of 450 V (optical length and electrode distance 1 mm) is 1:250, a value which is sufficient for many applications but can be optimized by further development of the ceramic fabrication technique.

This new transparent ceramic material is especially suitable for electro-optical devices which require high frequency switching, e.g. non-impact printers. The switching currents which are low compared to PLZT ceramics are advantageous for the lay-out of the driver circuits and for the life-time of the electrode patterns.

Principle aspects of chemical and physical properties of the material as well as the outline of the preparation technique will be described. The optical and electrical data will be given in detail.

SPECIFIC FEATURES OF HOLOGRAPHIC RECORDING IN TRANSPARENT FERROELECTRIC CERAMICS

A.E.Krumins and J.A.Seglins

Institute of Solid State Physics, Latvian State University, 226063 Riga, USSR

PLZT-9.2 transparent ferroelectric ceramics exhibits defect-induced photoconductivity which is responsible for its photorefraction under the applied field. The compound being in a metastable state at room temperature exhibits a quadratic electro-optic effect.

Due to the quadratic dependence of $\Delta n(E)$ it is possible to control the diffraction efficiency of these materials through the applied field E /I/. Recently it has been shown that the hologram forming in PLZT is followed by a considerable stationary energy exchange between the recording beams which is characterized by an extremely high gain $\Gamma \approx 120\ cm^{-1}$ /2/. To explain the effects observed in /2/ it is necessary to assume that quasi-neutrality does not hold under the applied field.

Presently an experimental test of the quasi-neutrality condition has been made. The variation of phase shift Ψ between the interference pattern snd holographic grating has been determined by the method described in /3/, and behaviour of Ψ under the applied field examined. It is shown that a bipolar diffusion of photocarriers occurs in PLZT-9.2.

The sensitivity S of hologram recording in PLZT-9.2 has been studied for the first time. The sensitivity is shown to be approximately a quadratic function of the applied field and to have a weak dependence on the holographic grating spacing (Λ) within the interval from 2 to 7 microns. The observed phenomena are well explained by the theory /4/ of the drift mechanism of the recording at $L \ll \Lambda = 2\ \mu m$, where L is the drift length of photocarriers. A steep drop of sensitivity at the transfer to $\Lambda = 1\ \mu m$ suggests that the drift length L becomes comparable to Λ.

1. Micheron F. et al. J.Amer.Ceram.Soc. 1974, vol.57, pp.306-308.
2. Butusov M.M. et al. Ferroelectrics, 1982, vol.45, pp.63-69.
3. Orlowski R., Krätzig E. Ferroelectrics, 1980, vol.26, pp.831-835.
4. Moharam M.G. et al. J.Appl.Phys., 1979, vol.50, pp.5642-5648.

NONHOMOGENEITY OF PHASE MODULATION BY PLZT RETARDATION PLATE

M. Ozolinsh, A. Kapenieks, and A. Krumins
Institute of Solid State Physics, Latvian State University
226063 Riga, USSR

This paper reports on the main factors causing temporal and spatial nonhomogeneities of phase modulation by electro-optic (EO) PLZT ceramics retardation plates (RP). The EO effect in PLZT 9.5-10/65/35 ceramics can be really switched on and off in few hundreds of nanoseconds, however a number of mechanisms of the EO effect in PLZT ceramics leads to varying of phase modulation in time within an interval up to hours. Besides during the interval comparable with periods of natural oscillations of the RP the nonhomogeneity of phase modulation is caused by the transient of electrostrictive deformations in the RP via the secondary EO effect. The specific contribution of the latter to the whole EO effect measured under dynamic conditions constitutes up to 40% for PLZT ceramics. It causes 12% or more than 50% nonuniformity of modulation in the amplitude modulators at the average retardation equal to a half-wave or quarter-wave, respectively, for the RP mounted so to be free to deform. It is shown how different ways of fixing the RP in order to damp the transient of electrostrictive deformations affect the nonuniformity of modulation as well as the controlling voltage.

The spatial nonhomogeneity in the real PLZT ceramics RP is caused mainly due to the electrically controlled light scattering; spatial distribution of the induced birefringence due to the nonuniformity of the controlling electric field; and interference effects in the birefringent PLZT ceramics RP. The contribution of the last mechanism exhibits a periodical dependence on the retardation of the RP with maxima and minima coinciding with the odd and even numbers of quarter-waves, respectively. The interference effects are evaluated by means of Jones formalisms, they should be taken into account in formation of Mueller's matrices in order to describe optical systems containing birefringent plates of PLZT ceramics. Contributions to the nonhomogeneity of all mentioned factors at the average retardations of the RP equal to a quarter-wave constitute: 0.02 - due to the interference effects, 0.006 - due to the nonuniformity of the induced birefringence, and 0.001 - due to the light scattering.

2:00 p.m. SESSION 3B: Piezoelectrics (Mechanical)
Chairman: A. Meitzler

3B-1 Properties, Structure, Modeling and Applications of Ferroelectric and Paraelectric PVDS Polymers (invited) - M. G. Broadhurst, National Bureau of Standards, USA

3B-2 Study on Shock Wave Explosive Energy Converter of PZT 95/5 Ferroelectric Ceramics - W. Yong-ling, Y. Wan-zong and L. Sheng-wei, Shanghai Institute of Ceramics, Peoples Republic of China

3B-3 High Pressure Shock Wave Arrival Detectors Utilizing Lithium Niobate - P.L. Stanton and R. A. Graham, Sandia National Laboratories, USA

3B-4 Anomalous Piezoelectric Current Pulses from Impact-Loaded Lithium Niobate - R. A. Graham and W. T. Brown, Sandia National Laboratories, USA

3B-5 Mechanical Properties of Grain Oriented Piezo-Ceramic with Bismuth Layer - and Tungsten-Bronze-Structure - H. Igarashi, M. Fujii, K. Nagata and K. Okazaki, National Defense Academy, Japan

3B-6 Influence of Mechanical Properties of Piezoceramics on Transverse Sensitivity - An Important Factor in Construction of Accelerometers - W. Wolny, Ferroperm, Denmark and T. R. Licht, Bruel & Kjaer Industry, Denmark

Structure, Properties, Modelling, and Applications of Ferroelectric and Paraelectric PVDF

Martin G. Broadhurst
National Bureau of Standards
Polymer Science and Standards Division
Washington, DC 20234

ABSTRACT

The ferroelectric β phase of PVDF results from the well known polar crystal packing of the molecules in the trans-planar conformation. By including comonomer units like trifluoroethylene in the molecule one can observe a transformation from the ferroelectric phase to a distinct paraelectric phase where the molecular conformation is disordered. Results of recent structural studies of these phases will be summarized.

With this structural knowledge in hand it is possible to make realistic models of the PVDF molecular and crystal structures. One such model is described. A much over simplified version of this model is analysed to show the varied and complicated behavior which one can predict for the ferroelectric/paraelectric phases of PVDF. Some of the predictions of the model are quantitatively compared to experimental property data for the polymer and parameters are evaluated. Finally examples will be given to demonstrate how the increased understanding gained from the above knowledge has been used to guide modification in the processing and structure of PVDF in order to improve its performance in particular applications.

Study on shock wave explosive energy converter of PZT 95/5 ferroelectric ceramics

Wang Yong-ling, Yuan Wan-zong, Lin Sheng-wei
(Shanghai Institute of Ceramics, The Chinese Academy of Sciences)

Abstract

Phase transition energy conversions have been developed in Shanghai Institute of Ceramics for several years with energy densities up to over 1 J/cm^3. From the static charge release-uniaxial stress curves of various ferroelectric ceramics, it shows that the phase transition effect will give greater contribution to the variation of polarization. In this paper several compositions of $Pb(Zr_{1-x}Ti_x)O_3$ type ceramics (X between .015 and .08) doped with Nb_2O_5 or Sb_2O_3 (denoted as ZT(Nb) and ZT(Sb) respectively) were prepared with Pr larger than 30 uc/cm^2 in ferroelectric state. The main physical properties of these ceramics are listed. Large size samples (160 × 80 × 10 mm) have been fabricated in our laboratory using conventional ceramic technologies. From the measuring curves of ϵ -T, DTA, temperature dependence of hysteresis loop and temperature dependence of pyroelectric coefficient, the composition-temperature phase diagram and shift of phase boundary with pressure and electric field are precisely determined.

The phase transition properties of Nb doped PZT 95/5 type ferroelectric ceramics under the action of shock-wave in "normal mode" condition have been investigated. In condition of parallel inductance-capacitance load, maximum current of 1360 A has been obtained. In condition of resistance load, maximum voltage of 145×10^3 V was obtained. All these results are in good agreement with theory.

High Pressure Shock Wave Arrival Detectors Utilizing Lithium Niobate*

by

P. L. Stanton and R. A. Graham
Sandia National Laboratories
Albuquerque, New Mexico 87185

Prior work[1] has demonstrated that Z-cut lithium niobate crystals produce very large output currents for impact pressures up to 90 GPa. The capability for response over such a large pressure range is a very desirable feature for a shock wave arrival detector. The present work investigates the use of lithium niobate as detectors for arrival times of explosively driven shock waves. The present work for crystals of much smaller diameter, and with less ideal loading than prior work shows outputs of tens of amperes for crystal diameters of from 1.3 to 3.8 mm. Although the output signals are less ideal than that of the prior work, time resolution of a few nanoseconds are indicated.

*This work performed at Sandia National Laboratories supported by the U.S. Department of Energy under contract # DE-AC04-76DP00789.

[1]P. L. Stanton and R. A. Graham, Appl. Phys. Lett. 31, 723 (1977).

Anomalous Piezoelectric Current Pulses from Impact-Loaded Lithium Niobate†

R. A. Graham and W. T. Brown
Sandia National Laboratories
Albuquerque, New Mexico 87185

When electrodes are placed on piezoelectric disks and connected to resistive circuits, current pulses of well-defined character are observed to be generated while the disks are subjected to controlled impact loading within the elastic range.[1] As the magnitude of the impact stress is increased substantial distortions may be observed in the current pulse. Certain of these distortions are electrical in character as they occur well within the elastic range. Details of such current pulse anomalies are described for Z-cut, Y-cut and 36-degree-oriented Y-cut lithium niobate crystals impact loaded in the elastic range. Similar observations are reported for Z-cut crystals subjected to pulse durations shorter than stress wave transit time. Residual strains in the crystals appear to have a significant influence on the current pulse anomalies. The anomalies are thought to be a consequence of either dielectric relaxation or dielectric breakdown.

1. L. Davison and R. A. Graham, Phys. Rep. 55, 255 (1979).

†This work performed at Sandia National Laboratories supported by the U. S. Department of Energy under contract # DE-AC04-76DP00789.

Mechanical Properties of Grain Oriented Piezo-Ceramics with Bismuth layer- and Tungsten-bronze-structures

H. Igarashi, M. Fujii, K. Nagata and K. Okazaki
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Yokosuka, 239 Japan

Abstract

Grain oriented $SrBi_2Nb_2O_9$ and $(Pb_{0.6}Ba_{0.4})_{0.97}La_{0.02}Nb_2O_6$ ceramics with various orientation factors were prepared by hot-pressing. A micro-indentation technique and a three point bend test were carried out on the grain oriented specimens, and the anisotropies in mechanical strength were discussed.

Crystallites of $SrBi_2Nb_2O_9$ with layer structure have a plate-like shape, and that of $(Pb_{0.6}Ba_{0.4})_{0.97}La_{0.02}Nb_2O_6$ with tungsten-bronze type have a lath-like shape. Therefore, the crystallites are aligned in the direction perpendicular to the hot-pressing direction. For the highly oriented specimens, an anisotrpy in crack length caused by micro-indentation was found. The cracks parallel to the hot-pressing direction were shorter than those of perpendicular. This asymmetric crack length increased with increasing of orientation factor. Fracture surfaces were examined by SEM.

Influence of Mechanical Properties of Piezoceramics on Transverse Sensitivity - an Important Factor in Construction of Accelerometers

Wanda Wolny,.....Industriselskabet FERROPERM A/S
.....Stubbeled 7 - DK-2950 Vedbaek
Torben R. Licht,..Bruel & Kjaer Industri A/S
..Skodsborgvej 307 - DK 2850 Naerum

Piezoceramics used in accelerometers are usually chosen because of their high charge or voltage sensitivity, stable temperature curve and low aging rate. Transverse sensitivity is a rather disturbing factor and can be diminished by special construction and careful mounting. Although of interest to manufacturers of accelerometers, dependence between mechanical properties of piezoceramics and transverse sensitivity has not been systematically tested. This report is based on several tests accomplished by means of commercial available accelerometers. Results shall show whether the right choice of ceramics can improve quality of accelerometers.

4:00 p.m. SESSION 4A: Pyroelectrics
Chairman: W. Schulze

4A-1 High Performance, Conducting Pyroelectric Ceramics (invited) - R.W. Whatmore, Plessey, UK

4A-2 Low Temperature Pyroelectric Properties - A. S. Bhalla and R. E. Newnham, The Pennsylvania State University, USA

4A-3 Tailored Spectral Response High Speed Pyroelectric Sensors - S.C. Stotlar and P.C. LeDelfe, Los Alamos National Laboratories, USA

4A-4 Pyroelectric/Silicon Hybrid Arrays for IR Sensors - R. Watton, Royal Signals Radar Establishment, UK

4A-5 Pyroelectric Property of $Pb(Sc_{1/2}Ta_{1/2})O_3$ Ceramics Under DC Bias - C. Zhili, Y. Xi and L. E. Cross, The Pennsylvania State University, USA

4A-6 Studies on Doped Triglycine Sulphate (TGS) for Pyroelectric Detector Applications - A. K. Batra and S.C. Mathur, Indian Institute of Technology, India

4A-7 Dielectric and Pyroelectric Properties of TGS-Polystyrene Composites - A. Mansingh and K. Sreenivas, University of Delhi, India

4A-8 Optimum Cuts of Monoclinic m Crystals for Pyroelectric Detector - A. Shaulov and W. A. Smith, Phillips Laboratories, USA

HIGH PERFORMANCE, CONDUCTING PYROELECTRIC CERAMICS

R.W. Whatmore
Plessey Research (Caswell) Limited
Allen Clark Research Centre
Caswell, Towcester, Northants, U.K.

ABSTRACT

Hot-pressed ceramics in the $PbZrO_3$ - Pb_2FeNbO_6 - $PbTiO_3$ system have been shown to possess a combination of pyroelectric, dielectric and mechanical properties which make them very suitable for use in pyroelectric infra-red detectors. The use of uranium as an off-valent dopant ion has been shown to give control of the electrical conductivity of ceramics in this system, which enables their electrical time constants to be determined and permits the elimination of high-value electrical bias resistors in the system. This paper will review the development of ceramics in this system and discuss their dielectric properties at frequencies down to 10^{-3}Hz. The relationships between dielectric loss and ceramic block defects will also be discussed.

Low Temperature Pyroelectric Properties

by

A.S. Bhalla and R.E. Newnham

Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16802

In the past, the major interest has been in the room temperature operating pyroelectric materials and relatively few pyroelectric measurements have been made at low temperatures. The low temperature pyroelectrics could be more efficient IR detectors as (1) ferroelectrics with low curie temperatures tend to show near second order behavior with large pyroelectric coefficients over wide temperature range. (ii) At low temperatures the secondary pyroelectric contribution which is often large and opposite in sign to the primary effect at room temperature, decreases rapidly and there can be unexpectedly large pyroelectric coefficients. (iii) Specific heat and electrical losses decrease at low temperature. (iv) Signal to noise ratio increases as temperature decreases. All these factors generally raise the figure of merit of the pyroelectric devices. In this paper we report the low temperature measurements of the pyroelectric and dielectric properties of several ferroelectric and non-ferroelectric materials and discuss the suitability of the pyroelectric material for device operation in the ambient conditions in the outer space.

TAILORED SPECTRAL RESPONSE HIGH SPEED PYROELECTRIC SENSORS

S. C. Stotlar and P. C. LaDelfe

Los Alamos National Laboratory

Over the past several years Los Alamos has developed high speed, improved response pyroelectric detectors for use in high flux, high speed applications in the infrared and ultraviolet. The materials suitable for use in such devices need to be rugged, nonhygroscopic, and sensitive. These include strontium barium niobate, lanthanum-doped lead zirconate, lithium tantalate, and lithium niobate. Other pyroelectric materials exhibit too low a sensitivity or Curie temperature (and thus depole) or are environmentally unstable. Unfortunately, these desirable materials are transparent and therefore unresponsive in the visible and near infrared. The ruggedness and speed of these detectors cannot be utilized for .5 μm, .9 μm, 1.06 μm, 3 to 5 μm and other wavelengths in the .4 to 5.6 μm region. This eliminates use with dye lasers (for most dyes), YAG, carbon monoxide, glass and other lasers which emit visible and near IR.

A method of tailoring the spectral response of energy (thermal) detectors in such a way that improvement in speed, sensitivity, and ruggedness (of the coating) results is reported.

This coating utilizes a thin film absorber, generally a partial absorber, and a modifier. This modifier couples the maximum energy into the absorbing layer which is very thin and chosen in material and thickness to retain very little heat. By using high index materials, the thickness required to absorb a large fraction of the heat is very small. As there remains a trade off between speed and sensitivity, multiple configurations can be used.

Coating design may require that the modifier and/or absorber may consist of several layers. While the absorber may typically be a metal, it is not a requirement. This technique permits the designer to tune the absorption, reflectance and transmission of the sensor and can provide narrow or broadband selective absorption. This method can be applied to face or edge type pyroelectric detectors and any thermal sensor. But because of its high speed potential, it will be most useful for fast pyroelectric detectors in providing visible - near IR response or enhancing the UV/IR response. As it can utilize photo-lithographic techniques, arrays and spectrophotometers can be developed.

High speed pyroelectric detectors have been designed and fabricated for use at 1.06 μm. Typical configurations, the method of design, and results of 50 MHz to 1 GHz tests will be reported.

Pyroelectric/Silicon Hybrid Arrays for IR Sensors

A Watton, RSRE Malvern, England.

In IR imaging, attention has recently been given to the solid state readout of very large arrays of uncooled detectors, particularly pyroelectrics. The aim is to produce arrays large enough such that there is a one to one correspondence of detector element to pixel in the image. With such formats the detector element bandwidth is reduced to less than 100 Hz. The result is that the moderate IR detectivity of the pyroelectrics has the potential for meeting a range of requirements. Devices from several hundred detector elements up to many thousands are of interest.

A suitable route for large two dimensional arrays is the pyroelectric/CCD hybrid. The design will be largely determined by considerations of the interface between the pyroelectric and the CCD, the three critical features being the efficiency of signal injection, the reduction of possible noise sources and the technology of flip-chip bonding. A theoretical analysis of the electrical and thermal interfaces has been developed to determine conditions for an efficient injection in the direct and indirect modes. The analysis has been extended to include the noise sources at the interface, and an examination made of the effects of aliasing. Critical design parameters have been identified. Experimental measurements on custom CCDs have verified the signal injection and noise analysis and a full design for a hybrid device has been completed.

Another format which is being considered is the long linear array of several hundred elements up to several thousands. There is more flexibility in the hybrid design due to the less restrictive geometry, and in particular noise aliasing may be reduced by IC buffer amplifiers. Design considerations include the low noise properties of the buffer and multiplexer combination.

Pyroelectric material aspects may be extracted from the design formulations and an examination has been made of relative material merit.

Pyroelectric Property of $Pb(Sc_{1/2}Ta_{1/2})O_3$ Ceramics Under DC Bias

Chen Zhili, Yao Xi and L.E. Cross

Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16802

It has been shown that quenched $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) disordered ceramics and crystals show diffuse dispersive dielectric properties, while well annealed ordered materials exhibit normal sharp first order ferroelectric transitions.

In this work, pyroelectric measurements by Byer-Roundy technique under DC biases up to 6 KV/cm within a temperature range from -80°C to 60°C have been studied. The results show that for both disordered and ordered materials, DC biases shift the peak of the pyroelectric coefficient towards higher temperature. However, for disordered samples the temperature shifts under DC bias are much larger than that for ordered ones. DC biases also sharpen the peak of the pyroelectric coefficient curve of the disordered samples. Clearly the depolarization curve shows a more abrupt phase transition behavior under DC biases.

Delay by the ordering electric field of the break-up of macro-domains into polar micro-regions under thermal motion is believed to be responsible for the extensive shifting and steepening observed in the depoling process under DC bias for the disordered samples.

Measurements by Chynoweth method under DC bias have confirmed that order-disorder of the polar micro-regions in them diffuse transition compositions is partly reversible and contributes a new extrinsic component to the pyroelectric response.

STUDIES ON DOPED TRI GLYCINE SULPHATE (TGS) FOR PYROELECTRIC DETECTOR APPLICATIONS

A.K. Batra and S.C. Mathur, Department of Physics, Indian Institute of Technology, Delhi, New Delhi - 110 016, India

A. Pandey, Department of Physics, Delhi University, Delhi-110 007, India.

It is now an established fact that the infrared detectors based on pyroelectric materials offer the advantage of room temperature operation and wide spectral response. A survey of a number of possible materials for use in pyroelectric detectors show that TGS and its derivatives are most promising. The major disadvantage of TGS is its tendency to depole near curie temperature. Attempts have been made to increase the curie temperature and check the depoling by doping TGS with L-alanine. This results in a biased hysteresis and better pyroelectric performance. But these crystals generally crack during the process of target preparation for use in IR detector applications. However, doping with inorganic ions make the crystal lattice rigid with no improvement in pyroelectric properties. It was, therefore, considered interesting to make an extensive study of doped TGS crystals that may lead to better operating characteristics to TGS or L-alanine doped TGS (LATGS). The dopants studied were amino acids, inorganic ions + L - alanine and dipolar organic impurities having NH_2 group. The properties investigated were pyroelectric coefficient, dielectric constant, ferroelectric transition temperature, and self-bias fields. Using these properties applicable pyroelectric figures of merit are calculated for comparison. It has been found that these crystals can be good target element and possess good mechanical properties for ease of target preparation. The merits and demerits of using these crystals are also discussed.

STUDIES ON DOPED TRIGLYCINE SULPHATE (TGS) FOR PYROELECTRIC DETECTOR APPLICATIONS

A.K. Batra and S.C. Mathur, Department of Physics, Indian Institute of Technology, Delhi, New Delhi - 110 016, India
A. Mansingh, Department of Physics, Delhi University, Delhi-110 007, India.

It is now an established fact that the infrared detectors based on pyroelectric materials offer the advantage of room temperature operation and wide spectral response. A survey of a number of possible materials for use in pyroelectric detectors show that TGS and its derivatives are most promising. The major disadvantage of TGS is its tendency to depole near curie temperature. Attempts have been made to increase the curie temperature and check the depoling by doping TGS with L-alanine. This results in a biased hysteresis and better pyroelectric performance. But these crystals generally crack during the process of target preparation for use in IR detector applications. However, doping with inorganic ions make the crystal lattice rigid with no improvement in pyroelectric properties. It was, therefore, considered interesting to make an extensive study of doped TGS crystals that may lead to better operating characteristics to TGS or L-alanine doped TGS (LATGS). The dopants studied were amino acids, inorganic ions + L - alanine and dipolar organic impurities having NH_2 group. The properties investigated were pyroelectric coefficient, dielectric constant, ferroelectric transition temperature, and self-bias fields. Using these properties applicable pyroelectric figures of merit are calculated for comparison. It has been found that these crystals can be good target element and possess good mechanical properties for ease of target preparation. The merits and demerits of using these crystals are also discussed.

DIELECTRIC AND PYROELECTRIC PROPERTIES OF TGS-POLYSTYRENE COMPOSITES

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Delhi - 110007
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ABSTRACT

A composite of triglycine sulphate (TGS) and polystyrene has been fabricated in a multilayer pattern with 2-2 connectivity made up of alternating layers of polystyrene and TGS powder. Samples with TGS powders of varying particle size, ranging from less than 75μm to more than 400μm were prepared in the form of thin sheets (2.0 cm x 1.5 cm x 0.15 cm). Samples with same weight percentage (70 to 75%) of TGS, but different particle size, were chosen for dielectric and pyroelectric studies in the ferro- and paraelectric phases. The dielectric constant and loss have been measured in the frequency range of 0.1 to 100 KHz and the pyroelectric current measurements were made by the Byer and Roundy direct method.

The magnitude of dielectric constant (ϵ') and pyroelectric coefficient P_y show an increase with increasing particle size and the room temperature values for the biggest particle size are [$\epsilon' = 8.3$] and $P_y = 0.6 \times 10^{-10}$ C cm^{-2} K^{-1} Anomalies in ϵ' and pyroelectric coefficient, indicating the existence of ferroelectricity were observed even for the composites with the lowest particle size of TGS ($< 75\mu$m). A dielectric dispersion in the frequency range 0.1 to 100 KHz and the particle size dependance of pyroelectric coefficient and dielectric constant can be accounted for by assuming non-ferroelectric surface layers at the bounderies of TGS crystallites. The responsivity of TGS-Polystyrene composites for infrared detection has been compared with those of single crystals, hot pressed TGS powders and composites employing other ferroelectrics. The decrease in pyroelectric coefficient with particle size is compensated to some extent by the decrease in dielectric constant, such that responsivity of these composites does not show any marked dependance on particle size.

OPTIMUM CUTS OF MONOCLINIC m CRYSTALS FOR PYROELECTRIC DETECTORS

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914-945-6000

Recently, an improved pyroelectric (PE) voltage responsivity has been demonstrated in crystals sliced at an oblique angle to the PE axis.[1] The crystals commonly studied belong to symmetry classes possessing an axis of rotation (2, 3, 4 or 6 fold). In such crystals the PE axis as well as a principal axis of the dielectric permittivity tensor must lie along the symmetry axis. However, this restriction is not imposed in crystals belonging to the monoclinic m and triclinic 1 classes.

In this paper we show that when the PE axis deviates from the principal axes of the dielectric tensor, the optimum oblique cut can produce much higher gains in the voltage responsivity. For example, in crystals with dielectric anisotropy ratio of 100, a gain of 5 is achieved when the PE axis is along the major principal axis; while the gain increases to 38 when the angle between these axes is 30°. The effect on the detectivity, D*, of detectors limited by Johnson noise is even more remarkable. When the PE axis is along the major principal axis of the dielectric loss tensor, an oblique cut can only decrease D*. However, if the angle between these axes is non-zero, say 40° for example, in a material with anisotropy ratio of 100, an optimum oblique cut can increase D* by a factor of 5.

[1] A. Shaulov, Appl. Phys. Lett. 39, 180 (1981).
A. Shaulov, W. A. Smith and N. V. Rao, Ferroelectronics 38, 967,

4:00 p.m. SESSION 4B: Piezoelectrics
Chairman: B. Jaffe

4B-1 PVF_2 Polymers: Ferroelectric Polarization and Piezoelectric Properties Under Dynamic Pressure and Shock Wave Action (invited) - F. Bauer, Inst. Franco-Allemand, France

4B-2 Measurement of Plantar Pressures Under the Human Foot Using Piezoelectric Ceramics (invited) - P.R. Cavanaugh and N. Macmillan, The Pennsylvania State University, USA

4B-3 Sandwich PZT/Polymer Composite Transducer - Z. Yong-qiu, H. Yuan-guang and X. Qi-chang, Academy Sinica, Peoples Republic of China

4B-4 The Piezoelectric Properties of Some PZT Composites - R.Y. Ting, Naval Research Laboratory, USA

4B-5 Perforated PZT Composites for Hydrophone Applications - A. Safari, S. DaVanzo and R.E. Newnham, The Pennsylvania State University, USA

4B-6 Transversely Reinforced 1-3 Piezoelectric Composites - M.J. Haun, T.R. Guruaja, W.A. Schulze and R.E. Newnham, The Pennsylvania State University, USA

4B-7 The Piezoelectric Properties of the Porous PZT and the Porous PZT Composite with Silicon Rubber - K. Hikita, K. Yamada, M. Nisioka and M. Ono, Mitsubishi Mining and Cement, Japan

PVF_2 POLYMERS: FERROELECTRIC POLARIZATION AND PIEZOELECTRIC PROPERTIES UNDER DYNAMIC PRESSURE AND SHOCK WAVE ACTION

F. BAUER

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Abstract

Polyvinylidene Fluoride PVF_2 presents a strong piezoelectric activity under specific conditions of cristallisation and polarization. PVF_2 is of particular interest. It combines the characteristic of a plastic material with those of a piezoelectric element. Study of the ferroelectric polarization and of the physical and piezoelectric characteristics and of its behavior under dynamic high pressure are of fundamental interest.

The piezoelectric and pyroelectric activities of PVF_2 depend on the polarization process as it is presented in the studies of the hysteresis loops P(E) (P: polarization, E: electrical field). The remanent polarization attains 10 $\mu C/cm^2$ for bi-axially stretched films from Rhône Poulenc Films. Results obtained on uniaxial stretched films from Pennwalt Corporation are also presented and discussed.

Properties under static pressure are presented. Applications to ballistic tranducers are described.

The dynamic behavior of piezoelectric PVF_2 under shock wave is surveyed. Study of shock loaded electric energy released from PVF_2 films will be reported. Results with PVF_2 transducers for weak or strong shock waves and applications of PVF_2 to shock pressure profile measurements are also reported. Investigation conducted at very high pressures level show that PVF_2 delivers electrical pulses which can be used in view of chronometric recording of strong shock waves and of shock pressure determination.

Conclusions on the variety of possible applications are given in which the ferroelectric characteristics of PVF_2 may find a widespread use.

Measurement of Plantar Pressures Under the Human Foot Using Piezoelectric Ceramics
(invited) P. R. Cavanaugh and N. Macmillan, The Pennsylvania State University, USA

(no abstract)

SANDWITH PZT/POLYMER COMPOSITE TRANSDUCER

Zhuang Yong-qiu, He Yuan-guang, Xu Qi-chang

(Institute of Acoustics, Academia Sinica, Beijing China)

Peoples Republic of China

This composite transducer consists of one PZT/polymer middle layer and two solid ceramic surface layers, basically. The PZT/polymer middle layer has 3-3 or 3-1 connectivity. Polymer may be silicone rubber, polyurethane and epoxy resin etc.. The solid ceramic surface layer facilitate to fire-on siliver electrode. This composite materials are characteriezed by IEEE standard on piezoelectric measurements.

(1) The electromechanical properties are affected by filling polymer or oil in 3-3 and 3-1 PZT ceramic framework. It shows that the hydrostatic piezoelectric coefficient g_h can not be increased by filling in polymer.

For 3-3 connectivity, as silicone rubber has filled, the parasitic vibration can be suppressed, the mechanical Q is decreased about from 12 to less than 8, the frequency constant N_t, dielectric constant ε, hydrostatic piezoelectric constant g_h, thickness electromechanic coupling K_t and standable hydrostatic pressure P_o have almost no change. For example, when porosity increased from 0.53 to 0.68, g_h is from 78×10^{-3} to 173×10^{-3}VM/N, ε is 400 to 200, and $d_h g_h$ is $47,000\times10^{-15}$ to $119,000\times10^{-15}$M /N, these properties are almost same either filling air or silicone rubber. As polyurethane filled, on the whole, it is similar to silicone rubber but N_t and P_o increase a little and g_h decrease very little. As epoxy resin filled, g_h decrease and N_t and P_o increase, obviously. As oil filled, g_h, N_t and P_o approximate to ordinary PZT's.

For 3-1 connectivity, similar experiments have made.

(2) g_h, K_t and N_t is affeced by thickness of solid ceramic surface layers for 3-3 connectivity. Experiments shows that g_h, K_t, N_t increase as the thickness decrease on the whole. For 3-1 connectivity, there is some difference.

(3) 3-1 PZT/polymer middle layer made with d=1.0mm, 0.8mm etc. diameter rods and porosity p=0.70-0.90 and the thickness ratio T of surface ceramic layer to total thickness is from 0 to 0.4, the electromechanical properties of these sandwith composite material is measured. For example, the sample with d=1mm, p=0.83, total thickness h=1.30mm, it's ε=238, K_t=0.67.

(4) Sandwith PZT/polymer transducers have been made for high sensitivity broadband hydrophone and ultrasonic medical transducer, the experiment results shows that it's performance is much better than ordinary transducer.

The Piezoelectric Properties of Some PZT Composites

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ABSTRACT

Lead zirconate-titanate (PZT) type ceramic has been widely used for sonar transducer applications for many years. But there is a constant need to improve its piezoelectric property. In recent years, the emphasis has been focused on the development of new PZT composite materials. The basic concept of the composite designs is to reduce the lateral bonding in PZT such that the contributions of d_{31} and d_{32} may be reduced. The resultant multi-phase PZT composites usually have a lower dielectric constant and higher hydrostatic figure-of-merit, when compared with bulk PZT itself.

Two types of PZT composites were recently characterized. The first is a coral-type PZT having a 3-3 connectivity, produced by using the replamine process developed by the Pennsylvania State University. The second type is an epoxy-PZT composite with a 2-3 connectivity. A reciprocity method was employed for measuring the hydrostatic piezoelectric constants at 1 kHz by using a castor-oil filled acoustic coupler. The properties evaluated included the dielectric constant, dissipation factor and the hydrostatic d_h and g_h constants. The effects of temperature, pressure and epoxy impregnation of the composites on their properties will be discussed.

PERFORATED PZT COMPOSITES FOR HYDROPHONE APPLICATIONS

A. Safari, S. DaVanzo and R.E. Newnham
Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16802

Macrosymmetry and interphase connectivity have been used to explore the possible macrostructures of interest for piezoelectric composites. Based on these design considerations, PZT-polymer composites with 3-1 and 3-2 connectivity patterns have been fabricated. These composites were prepared by drilling circular and square holes perpendicular to the poling direction in prepoled PZT blocks and filling the holes with epoxy. The influence of hole size, separation between the holes and thickness on the piezoelectric properties of the composites was studied. An enhancement in the piezoelectric $\bar{d}_h$ coefficient was observed due to the decoupling of the piezoelectric $\bar{d}_{33}$ and $\bar{d}_{31}$ coefficients in the composites. The dielectric constant of PZT is lowered considerably because of the polymer phase. The combination of high $\bar{d}_h$ and low dielectric constant results in greatly enhanced $\bar{g}_h$. For hydrophone applications, these composites give good acoustical matching with water because of their low density.

A theoretical analysis was made to calculate internal stress distribution and local polarization in order to understand the enhancement of $\bar{d}_h$ and $\bar{g}_h$. The finite element method (FEM) was used to calculate the internal stress distribution inside the composites under hydrostatic loading. The local and remanant polarization and piezoelectric matrix were calculated. From these data the macroscopic piezoelectric coefficients $\bar{d}_h$ and $\bar{g}_h$ of the composites were calculated.

Transversely Reinforced 1-3 Piezoelectric Composites

M.J. Haun, T.R. Gururaja, W.A. Schulze and R.E. Newnham

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University Park, PA 16802

Piezoelectric PZT-polymer 1-3 composites were transversely reinforced to increase the hydrostatic piezoelectric coefficients for possible use in hydrophone applications. These composites were made of a polymer matrix with PZT rods aligned in the poling direction (χ_3) and reinforcement in the transverse directions. The reinforcement consisted of aligned glass fibers and/or a rigid encapsulation. Both types of reinforcement act to greatly decrease the piezoelectric $\bar{d}_{31}$ coefficient by carrying most of the lateral stresses. The $\bar{d}_{33}$ coefficient is relatively unaffected, because PZT rods carry most of the stress in the poling direction. This decoupling of the $\bar{d}_{31}$ and $\bar{d}_{33}$ coefficients enhances the hydrostatic piezoelectric $\bar{d}_h$ coefficient. The effect of the glass fibers is dependent on the polymer matrix used. Because of the stiffness of many epoxies, no significant increase in $\bar{d}_h$ results, but more compliant polyurethanes are significantly reinforced giving improved $\bar{d}_h$ coefficients. Due to the differences in poisson's ratios and compliances of PZT and the polymer matrix, adverse internal stresses develop which can contribute to the $\bar{d}_{31}$ coefficient. To lower the $\bar{d}_{31}$ coefficient the polyurethane is foamed, in addition to adding glass fibers, which lowers the poisson's ratio, and reduces the internal stresses. Greater hydrostatic sensitivity is achieved by foaming polyurethane, but only at low pressures. At higher pressures the pores begin to collapse and the polymer stiffens, lowering the sensitivity of the composite. This pressure dependence can be greatly reduced by encapsulating the composite in epoxy. The epoxy encapsulation also prevents penetration of the liquid medium into the porous composite, as well as providing additional transverse reinforcement. Due to the small

percentage of PZT used, these composites have densities near that of water, and much lower dielectric constants than solid PZT, resulting in large increases in the piezoelectric $\tilde{g}_h$ coefficient. By increasing $\tilde{d}_h$ and $\tilde{g}_h$, the $\overline{d_h g_h}$ product used as the figure of merit, is greatly enhanced.

THE PIEZOELECTRIC PROPERTIES OF THE POROUS PZT AND THE POROUS PZT COMPOSITE WITH SILICON RUBBER

K. Hikita, K. Yamada, M. Nisioka and M. Ono

Mitsubishi Mining & Cement Co., LTD
Reserch & Development Lab.
Yokoze Chichibu-Gun Saitama-ken 368 Japan.

The porous PZT ceramics and the porous PZT composites with silicon rubber were fabricated to produce a high sensitive transducer, and the piezoelectric properties along the poling direction related with the porosity were investigated.

The porous PZT ceramics that the composition was $Pb(Zr\ 0.53, Ti\ 0.47)O_3$ with 0.75wt % Nb_2O_5 were prepared by a conventional producing method, and the porosity of them were up to about 70 volume %.
As the porosity was increased more than 70 vol%, the PZT ceramics became too brittle to handle.
The porous PZT composite with silicon rubber was made by filling the void with silicon rubber.

The piezoelectric properties were measured by the resonant and antiresonant frequencies for the porous PZT ceramics and the composite.
As the porosity was increased, the d_{33} coefficient measured by resonant-antiresonant frequencies had a tendency to increase and the permittivity tended to decrease linearly. Consequently, g_{33} coefficient was increased with porosity, and was about 200 x 10^{-3}(Vm/N) for the porosity of 60%, and some of the g_{33} coefficients were over 500 x 10^{-3}(Vm/N) for the porosity of 70%.

The d_{33} coefficient for the flexible transducer that the ceramic structures of the composite were destroyed was measured using a d_{33} meter, and was not half so large as that before destruction.
The g_{33} was decreased after destruction of ceramic structures, even though the permittivity was decreased.

8:45 a.m. SESSION 5A: Materials (General)
Chairman: R. Gerson

5A-1 Synthesis, Properties and Applications of Ferroelectric Smectic Liquid Crystals (invited) - J.W. Goodby, Bell Laboratories,USA

5A-2 Ultrafine Electroceramic Powder Preparation from Metal Alkoides (invited) - Y. Ozaki, Seikei University, Japan

5A-3 Aluminate-Sodalite $Sr_8(al_{12}O_{24})(CrO_4)_2$ - A New Ferroelectric Material - N. Setter, W. Depmeier and H. Schmid, University of Geneva, Switzerland

5A-4 Polar Behavior of the Platinum/Zirconia Interface - A. H. Meitzler, Ford Research Laboratory, USA

5A-5 Composition, Structure and Properties of Ferroelectrics - A. Bussmann-Holder and H. Bilz, Max Planck Institute, Federal Republic of Germany

5A-6 The Effect of 0.039 Atomic Percent Niobia on the FE_1-FE_2 Phase Transition in the High $PbZrO_3$ Region of the System $PbZrO_3$ - $PbTiO_3$ - K. O. Starcher, General Electric Company, USA

5A-7 Photolithographic Etching of TGS - D.C. Wang, J.S. Shie and S.S. Chen, National Chiao Tung University, Taiwan

SYNTHESIS, PROPERTIES AND APPLICATIONS OF FERROELECTRIC SMECTIC LIQUID CRYSTALS

by

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ABSTRACT

Although smectic liquid crystals containing an optically active center were first prepared over fifty years ago, it was only realized recently that a number of these materials were ferroelectrics. Smectic phases which exhibit ferroelectric properties have structures in which their optically active molecules have their long axes tilted with respect to the layer planes of the phase. Smectic phases C^*, I^*, F^* and possibly G^* and G'^* possess these properties. The synthesis of ferroelectric liquid crystal materials, the subsequent identification of their phases, and the blending of these materials in order to obtain a stable smectic phase at room temperature will be discussed. The use of these types of liquid crystal phase lies in their bistable nature and fast switching speeds in electrooptic display applications. Some novel display techniques will be described.

Ultrafine Electroceramic Powder Preparation from Metal Alkoides

Yoshiharu OZAKI
Seikei University, Kichijoji Kitamachi 3,
Musashinoshi, Tokyo 180, Japan

A great interest in the electronic industries is to realize a size reduction of electronic components without a lowering of the quality, reliability and cost performance. The utilization of metal alkoides is one of the potential method for realization of these requirement.

Metal alkoides are synthesized by the reactions of metals or metal chlorides with an alcohol. And metal alkoides are hydrolyzed to ceramic powders or ceramic precursor powders. These reactions procced at very low temperature in the range from room temperature to about 100°C, and give ultrafine, monodispersed and compositionally homogenous powder particles. They realize the production of high quality, high reliable electroceramics.

My presentation will contain as follows:

1. Trends of technology in materials science
2. Cases of the microstructure design
3. State of the electroceramic powder preparation from solution
4. Potentials of metal alkoides for advanced electroceramics
5. Practical application of alkoxy-derived powder for electronic components

1. Crystalline powder

1.1. Oxide powder

$BaTiO_3$, $CaTiO_3$, $BaZrO_3$, $Ba(Ti,Zr)O_3$, $Sr(Ti,Zr)O_3$
$(Ba,Sr)TiO_3$, $(Ba,Sr)ZrO_3$, Zn_2GeO_4, $ZnFe_2O_4$, $BaWO_3$

1.2. Hydroxide or Oxide hydrate

$BaSnO_3$, $SrSnO_3$, $MgSnO_3$, $CaSnO_3$, $PbSnO_3$, $BaGeO_3$,
$SrGeO_3$, $PbGeO_3$,

2. Amorphous powder

$MgTiO_3$, $CaTiO_3$, $PbTiO_3$, $PbZrO_3$, $Pb(Zr,Ti)O_3$, $(Pb,La)(Zr,Ti)O_3$, $Ba(Zn_{1/3}Nb_{2/3})O_3$, $Sr(Zn_{1/3}Nb_{2/3})O_3$, $Sr(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Sr(Zn_{1/3}Ta_{2/3})O_3$, $Sr(Mg_{1/3}Ta_{2/3})O_3$, $Ba(La_{1/2}Ta_{1/2})O_3$, $Ba(Y_{1/2}Ta_{1/2})O_3$, $Ba(Gd_{1/2}Ta_{1/2})O_3$, $Ba(Eu_{1/2}Ta_{1/2})O_3$, $RAlO_3$(R=Y,La,Nd,Sm,Eu,Gd,Tb), $R_3Al_5O_{12}$(R=Y,Nd,Eu,Gd,Tb), $RFeO_3$(R=Y,La,Nd,Sm,Eu,Gd,Tb), $R_3Fe_5O_{12}$(R=Y,Nd,Eu,Gd,Tb), $LnInO_3$(Ln=La,Sm,Nd), $SrZrO_3$, $ZrTiO_4$, $NiFe_2O_4$, $CoFe_2O_4$, $CuFe_2O_4$, $MgFe_2O_4$, $(Ni,Zn)Fe_2O_4$, $(Co,Zn)Fe_2O_4$

Aluminate-Sodalite $Sr_8(al_{12}O_{24})(CrO_4)_2$ - A New Ferroelectric Material

N. Setter, W depmeier, and H. Schmid
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Single crystals of strontium-chromate aluminate-sodalite have been grown by the flux method. A first order ferroelectric phase transition occurs at287^{o}K (upon cooling).ε'_{max}=90, $\varepsilon'_{300^{o}K}$=13, and $D_{300^{o}K}\leq$0.0001 for frequency range 1 to 1000 kHz. Ferroelectric properties and a potential pyroelectric application will be discussed as well as extension to other members of the aluminate-sodalite family.

POLAR BEHAVIOR OF THE PLATINUM/ZIRCONIA INTERFACE

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Ford Motor Company
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ABSTRACT

Experimental evidence indicates that Pt electrodes sputter-deposited on the surfaces of Y_2O_3-doped ZrO_2 ceramics form interfacial layers with polar properties. If a sample of Y_2O_3-doped ZrO_2 ceramic with sputter-deposited Pt electrodes is cooled down from 500° C with a potential difference of 1.0 volt applied to the electrodes, the sample, when reheated, will show a pyroelectric discharge current that starts around 200° C, peaks around 300° C, and returns to zero around 500° C. The total discharge has been measured for a number of samples by recording the voltage drop across a 1.0 megohm resistor connected to sample electrodes as the sample temperature was ramped up over a period of approximately one hour. If interpreted as caused by a dipole interfacial layer, the discharge is equivalent to a polarization of approximately 80 $\mu C/cm^2$. The polarity of the discharge current can be reversed by applying a voltage of opposite polarity during cool down. If the sample is cooled down from 500° C with electrodes short-circuited, no discharge current is obtained when the sample is reheated. Thus in many respects, a sample behaves like a ferroelectric ceramic sample with a pyroelectric discharge current dependent upon poling conditions; however, no polar bulk effects like piezoactivity have been observed.

The same pyroelectric discharge currents observed to be present in disc-shaped samples of Y_2O_3-doped ZrO_2 with Pt electrodes have been observed in a number of samples of commercially manufactured, automotive, exhaust-gas-oxygen sensors using Y_2O_3-doped ZrO_2 ceramic and Pt electrodes. This paper reports experimental results from both types of samples and an analytical model, all of which support the conclusion that a layer with polar properties exists at the Pt/ZrO_2 interface.

COMPOSITION, STRUCTURE AND PROPERTIES OF FERROELECTRICS

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Ferroelectric materials of the displacive type show a strong interrelation between chemical composition and properties. Most of them are ternary or more complex chalcogenides except for a few IV-VI compounds. They usually exhibit structures of high (cubic or hexagonal)symmetry in their paraelectric phases. It is shown that in a polarizability model (refer to the included preprint) the transition temperature T_c depends on three local microscopic parameters which correlate strongly with the chemical constituents but are rather independent of the structure of ferroelectrics. The model describes thermodynamic and dynamic properties of ferroelectric materials quite well in a self-consistent phonon approximation. A non-linear extension of the model is used to discuss non-linear phenomena of ferroelectrics , such as the photo-induced properties.

THE EFFECT OF 0.039 ATOMIC PERCENT NIOBIA ON THE FE_1-FE_2 PHASE TRANSITION IN THE HIGH $PbZrO_3$ REGION OF THE SYSTEM $PbZrO_3$ - $PbTiO_3$

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ABSTRACT

The PZT perovskite structure accommodates a copious amount of ionic substitution. Nb_2O_5 is often used as a dopant (up to 0.02 atomic percent) in PZT to increase the volume resistivity and domain wall mobility of the ceramic. Both of these effects are beneficial during poling of PZT where the ceramic must withstand high voltage and the domains are aligned with the poling field.

In this study, high Zr^{4+} containing $Pb(Zr,Ti)O_3$ (PZT) ceramic samples, doped with approximately 0.039 atomic percent niobia, were prepared and tested to determine the effect of the niobia on the FE_1-FE_2 phase boundary and other selected properties. Data from the seven compositions studied indicate the following effects of 0.039 atomic percent niobia dopant (versus PZT with no niobia).

- Increases the FE_1-FE_2 transition temperature (approximately 30°C for PZT 93/7).
- Increases the hydrostatic depoling pressure required to cause the ferroelectric-to-antiferroelectric transition (by more than 30,000 lb/in^2 for PZT 95/5).
- Increases the remanent polarization (by approximately 15 $\mu coul/cm^2$ for PZT 93/7) and decreases the coercive field (by approximately 1 kV/in. of sample thickness for PZT 95/5).
- Increases the piezoelectric coefficient d_{33} (by approximately 14 x 10^{-12} coulomb/newton for PZT 93/7).

PHOTOLITHOGRAPHIC ETCHING OF TGS

D. C. WANG, J. S. SHIE and S. S. CHEN

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Oct. 25, 1982

Abstract — The solubility and the etching rate (b-face) of triglycine sulfate crystal in acetone- and ethyl alcohol-water solutions were studied. It has been found that both vary activationally with respect to the solution temperature, and exponentially to the water volume concentration. By combining the etching method with the photolithographic technique used in semiconductor device fabrication, it is feasible to make TGS pyroelectric detectors of select-etched structures, which, comparing to the conventional ion-milling technique, is advantageous in processing handling and tooling, together with high sensitivity of detectors resulting from the controllable thinner thickness and the better thermal insulation of the detector active area. Accurate controllability of the etched depth within ±10% can be easily achieved in our experiment using very simple facilities and ethyl alcohol-water solution at $0^{o}C$. The results of the study are used to fabricate TGS pyroelectric point detector of self-supporting structure with high responsivity obtained.

8:45 a.m. SESSION 5B: Piezoelectrics (Hydrophones, Composites, Bimorphs)
Chairman: D. Berlincourt

5B-1 Recent Developments of Piezoelectric Ceramic Products and Composites of Synthetic Rubber and Piezoelectric Ceramic Particles (invited) - H. Banno, NTK-NGK, Japan

5B-2 Recent Measurements on Improved Thick-Film Piezoelectric PVdF Polymer Materials for Hydrophone Applications (invited)- J.C. McGrath, EMI, UK

5B-3 Unconventional Methods for Poling Hard PZT - T.R. Shrout, A. Safari, P. Moses and W.A. Schulze, The Pennsylvania State University, U.S.A.

5B-4 Optomechanical Bimorph Actuator - P.S. Brody and J. O. Gurney, Jr., Harry Diamond Laboratories, USA

5B-5 The Incorporation of Rigid Composites into a Conformal Hydrophone - W. Schulze and Staff, The Pennsylvania State University, USA

5B-6 Application of Tubular PVF_2 to Shock Resistant Hydrophone - T.A. Henriquez and A.C. Tims, Naval Research Laboratory, USA

5B-7 Glass-Ceramics: New Materials for Hydrophone Applications- A. Halliyal, A. Safari and A.S. Bhalla, The Pennsylvania State University, USA

PIEZOELECTRIC PROPERTIES OF COMPOSITES OF SYNTHTIC RUBBER AND $PbTiO_3$ OR PZT

H. Banno and S. Saito
NTK Technical Ceramic Division
NGK Spark Plug Co., Ltd.
14-18, Takatsuji-cho, Mizuho-ku, Nagoya, Japan 467

The piezoelectric properties, particularly those important for hydrophone application, of flexible composites of synthetic rubber and piezoelectric ceramic particles are reported in this paper. Also a theoretically derived " modified " cubes model is presented, which generalizes the parallel, series and cubes models.

1. Introduction

In recent years, the hetro-structure materials, such as composites of ceramics and polymers, have attracted much interest because of the limitation of the performance of single phase materials.

Early attempts to make the flexible composites of piezoelectric ceramic particles and polymers were made by Kitayama et al. [1] in Japan and Pauer [2] in the United States. In 1975, Harrison[3] measured and reported the dielectric and piezoelectric constants of the composites of PZT particles and silicone rubber.

The theories on the dielectric permittivity of the composites have been reviewed by Pauer [2] based on series, parallel, maxwell's and cubes models. Using the spherical model, the dielectric and piezoelectric constants have been derived by Furukawa et al.[4]

In 1978, the concept of connectivity was introduced by Newnham et al. [5] and the theory on the piezoelectric constants of the composites was developed based on the series and parallel models.

In this paper, the piezoelectric properties, particularly those important for hydrophone application, of the composites of synthetic rubber and piezoelectric ceramic particles of $PbTiO_3$ or PZT are reported and also a theoretically derived " modified " cubes model is presented, which generalizes the parallel, series and cubes models.

2. Theory

The composites of ceramic particles (phase 1) and polymers (phase 2) have a 3-0 microstructure as described by Newnham et al. [5] A composite with 3-0 connectivity is shown in Fig. 1 (a). A unit cell of the composite is shown in Fig. 1(b) with a relation:

$$[a+(1-a)\ell][a+(1-a)m][a+(1-a)n] = 1 \qquad (1)$$

where $0 < a \leq 1$, $0 \leq \ell$, $0 \leq m$ and $0 \leq n$.

We can assume $\ell = m$ in the case of the ceramic particles-polymers composites because they are made into sheets as described below. As shown in Fig. 2, we obtain a unit cubes cell equivalent to the unit cell illustrated in Fig. 1(b).

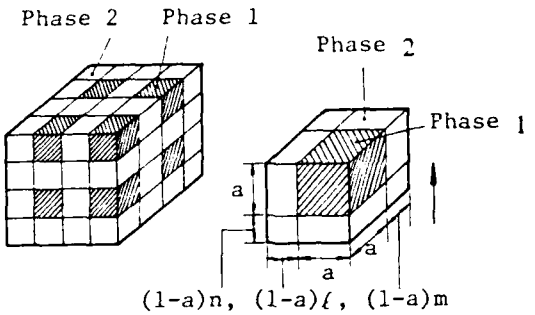

Fig. 1(a) A composite with 3-0 connectivity and (b) a unit cell of the composite

This cubes model, which we will call a " modified " cubes model, becomes equivalent to the parallel, series and cubes models in the cases when n=0, m=0 and m=n=1, respectively. This cubes unit may be divided into two parts as shown in Fig. 3.

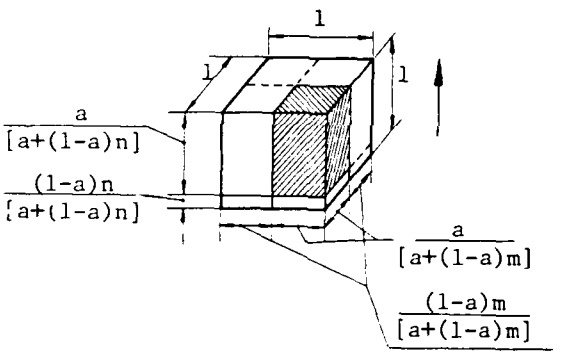

Fig. 2 A unit cubes cell equivalent to the unit cell illustrated in Fig. 1 (b)

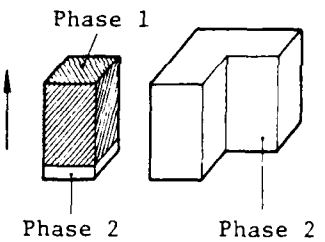

Fig. 3 Schematic representation for the modified cubes model

Based on this geometry and by uniting a series and parallel models, we can derive the theory on the dielectric and piezoelectric constants. The equations based on series and parallel models have been derived by Newnham et al. [5] Following the notations used by Newnham et al. [5] and assuming that ${}^{1}d_{33} >> {}^{2}d_{33}$, ${}^{1}d_{31} >> {}^{2}d_{31}$, ${}^{1}s_{33} << {}^{2}s_{33}$ and ${}^{1}s_{11} << {}^{2}s_{11}$, the theoretical equations based on our " modified " cubes model become as follows:

$$\bar{\epsilon}_{33} = \frac{a^2 \cdot [a+(1-a)n]^2 \cdot {}^{1}\epsilon_{33} \cdot {}^{2}\epsilon_{33}}{a \cdot {}^{2}\epsilon_{33} + (1-a)n \cdot {}^{1}\epsilon_{33}} + \left\{1 - a^2 \cdot [a+(1-a)n]\right\} \cdot {}^{2}\epsilon_{33} \qquad (2)$$

$$\overline{d}_h = \frac{{}^1d_h}{(1-2\cdot{}^1\alpha_i)} \cdot \frac{a^3\cdot[a+(1-a)n]}{a+(1-a)n\cdot({}^1\epsilon_{33}/{}^2\epsilon_{33})} \cdot \left\{ \frac{1}{\frac{(1-a)n}{a+(1-a)n}+a^3} - 2\cdot{}^1\alpha_i \right\} \quad (3)$$

and $\overline{g}_h = \overline{d}_h / \overline{\epsilon}_{33}$

where ${}^1\alpha_i = -{}^1d_{31}/{}^1d_{33} = -{}^1g_{31}/{}^1g_{33}$

which is a kind of anisotropy factor of 3-1 and 3-3 in the piezoelectric constants.

3. Experiments

The samples were prepared in the following ways. The piezoelectric ceramic particles of Bi_2O_3-modified $PbTiO_3$ (MPT) and WO_3-modified $Pb(Zr,Ti)O_3$(MPZT) were made by grinding the sintered ceramics, while those of pure $PbTiO_3$ (PPT) were made by water quenching.

The piezoelectric ceramic powders and synthetic rubber (chloroprene rubber) were mixed and rolled down into about 0.5 mm thich sheets at 40 °C using a hot roller, and then heated at 190 °C for 20 min. under the pressure of 13 kg/cm^2. The conductive paste (Fujikura Chemical-Dotite D-500) was attached on the both sides of the specimens as electrodes. Then the specimens were polarized at 60 °C in silicone oil by applying a DC field of 100 kV/cm for 1 hour.

The dielectric permittivity was measured with a capacitance bridge at 1 kHz. The piezoelectric constants for hydrophone, d_h and g_h, were measured according to a similar method described by Pauer [2].

The piezoelectric ${}^1d_{33}$ and ${}^1d_{31}$ constants were measured according to the IRE standards method.

The average particle size of ceramic powder was measured by Sub-sieve-sizer.

4. Results and discussion

Figs. 4 and 5 show the dielectric ($\overline{\epsilon}_{33}$) and piezoelectric ($\overline{d}_h$) constants of the MPT, PPT and MPZT as a function of volume fraction of the ceramic particles.

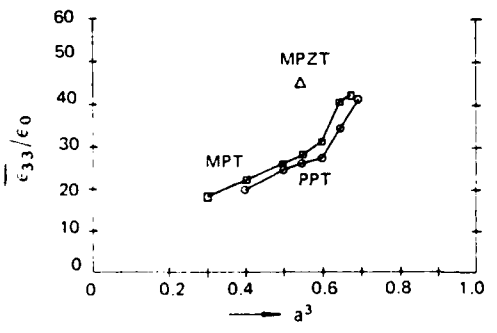

Fig. 4 $\overline{\epsilon}_{33}/\epsilon_0$ vs. a^3

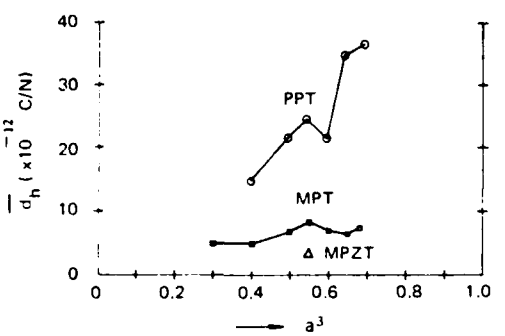

Fig. 5 $\overline{d}_h$ vs. a^3

From these results, the n values for $\bar{\epsilon}_{33}$ and $\bar{d}_h$ can be calculated using eqs. (2) and (3) and the values ${}^1\epsilon_{33}/\epsilon_0 = 300$, ${}^2\epsilon_{33}/\epsilon_0 = 7.3$, ${}^1d_h = 49.5 \times 10^{-12}$C/N and ${}^1\alpha_i = 0.18$. The calculated n values for $\bar{\epsilon}_{33}$ and $\bar{d}_h$ for the MPT are plotted in Fig. 6, which shows a good correlation between the two.

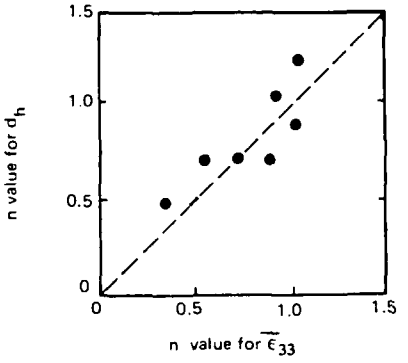

Fig. 6 Correlation between n values for $\bar{\epsilon}_{33}$ and $\bar{d}_h$ for MPT

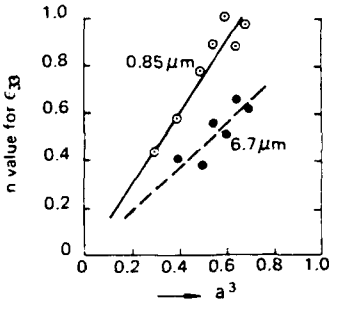

Fig. 7 n values for $\bar{\epsilon}_{33}$ as a function of volume fraction of MPT for two different particle sizes

The dielectric and piezoelectric constants of the PPT have not been obtained due to the difficulty in obtaining dense sintered body. However, using the data for the PPT composites, we can determine these constants. Fig. 7 shows the n values for $\bar{\epsilon}_{33}$ as a function of volume fraction of ceramics for two different particle sizes. It is seen that the n values are larger for the smaller particle size, which is considered due to the difference in the surface areas.

5. Summary

Good agreement between the " modified " cubes model and the experimental results was obsered. Pure $PbTiO_3$ showed the best properties for the hydrophone application among the ceramic particles studied when they were made into the flexible composites with the synthetic rubber.

We wish to thank Messrs. T. Yamamoto and A. Itani for sample preparation, Mr. N. Wakita for computer calculation and Dr. Y. Tajima for help in preparation of this manuscript.

References

1) T. Kitayama and S. Sugawara; Rept. Prof. Gr. Inst. Elec. Comm. Eng. Japan. CPM72-17 (1972), (in Japanese)
2) L. A. Pauer; I.E.E.E. Int'l Conv. Rec., 1973 p1-5 (1973)
3) W. B. Harrison; Proc. Workshop on Sonar Transducer Materials, Naval Res. Labs. p257, Nov. 1975
4) T. Furukawa, K. Ishida and E. Fukada; J. Appl. Phys.50, 7 p4904-4912 (1979)
5) R. E. Newnham, D. P. Skinner and L. E. Cross: Mat. Res. Bull. 13, p525-536 (1978)

Recent Measurements on Improved Thick Film Piezoelectric PVDF Polymer Materials for Hydrophone Applications (invited) - J.C.McGrath, EMI, UK

(no abstract)

Unconventional Methods for Poling Hard PZT

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Recently improved methods for poling PZT has been reported. Shrout et al.[7] reported that due to their inherent high electrical resistivity donor doped or 'soft' PZTs could be poled using the field cooling methods, i.e. apply DC field while cooling through T_c. The electric fields required were reduced by a factor of five as compared to fields required for conventional poling. Another novel method for poling was reported by Bindal and Singh[2] in which poling was performed by applying a large dc field (conventional method) during which the samples were maintained in a vibrating condition using a small ac field at the resonant frequency. An increase in the piezoelectric d_{33} was observed in the case of acceptor doped or "hard" PZTs. No other properties were reported. In this investigation, disks of a commercially available 'hard' PZT were poled using the field cooling method, however, due to their inherent low resistivity the field was applied in short pulses (pulse poling) while the samples were cooled through T_c. Samples were also poled using the vibrating method mentioned above. A comprehensive study of the two poling methods included the determination of the dielectric constant, piezoelectric d_{33}, coupling coefficients, mechanical Q, ac depoling field and ageing characteristics. The piezoelectric properties for both poling methods were found to be improved as compared to those of conventionally poled samples.

1. T.R. Shrout, A. Safari and W.A. Schulze, Ferroelectrics Letters (in press).
2. V. Bindal and J. Singh, Ferroelectrics 41, 179 (1982).

OPTOMECHANICAL BIMORPH ACTUATOR

by

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The cross coupling of optically produced voltages and piezoelectric constriction and expansion has been used to construct a bimorph structure mechanical actuator which is driven by illummating the lateral surfaces of the thin sheet structure. The bimorph is constructed from fine grained P2T-5A, sheet stock material which is strongly piezoelectric and which also exhibits a large high-voltage bulk-like photovoltaic effect. The deflection is proportional to the total optical energy input, saturating at a magnitude dependent on the photovoltaic saturation emf. The deflectional velocity is proportional to the illimination intensity. The motion is away from the illumination source.

Very simple structures 20mm long, 5.7mm wide and 0.33 mm (total) in thickness were fabricated. Broud-band UV illumination centered at 375 nm produced a tip deflection of 0.33 mm for an input of 7 mJ.

We develop formulae for deflection and deflectional velocity and also for the total force applied by a clamped element. We describe a proposed application of the device as an optically driven mechanical gas flow modulation element internally mounted in the gainblock of a fluidic amplifier. Such a device would be an "optical to flow" transducer for control applications.

The Incorporation of Rigid Composites into a Conformal Hydrophone

Walter Schulze, Gordon Dayton, Deborah Laubscher, Linda Webster,
Esse Bibeau, Rebecca Miller, B. Joseph Kearns, S. Richard Brenneman,
Daniel Cross, Michael Haun, Amnuay Narthasilpa, Beth Jones,
Ahmad Safari, Thomas Shrout, Sui-Yuan Lynn, Robert Wilson and James Biggers

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During the past five years, numerous composite configurations have been analysed for hydrostatic transducer application. Although some of these designs have been flexible, a configuration with good sensitivity and mechanical durability has not been produced. The need for a sheet or mat, large area transducer that will conform to the hull of a ship has led to the incorporation of small rigid composite elements into a macrocomposite. The goals set for the conformal transducer were sensitivity greater than -200 dB re 1 V/μPa, operation to at least 7 MPa, maximum frequency of 100 kHz, conforming to a 0.10 m radius and a hydrophone section of at least 0.01 m^2.

In the study three types of rigid composites are used to determine the effect of compliant hinge material and flexible electrodes on the hydrostatic sensitivity. Typical response of a 1-3 rod composite in flexible form is a sensitivity of -193 dB re 1 V/μPa, with a capacitance of 14 μf per m^2 and only 2 dB degradation when operating at 7 MPa.

Application of Tubular PVF_2 to a Shock Resistant Hydrophone

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A. C. Tims
Naval Research Laboratory, USA

Polyvinyldiene fluoride (PVF_2), a polymer with the capability of retaining a piezoelectric polarization, has been shown to have certain advantages over traditional piezoelectric materials in the design of underwater acoustic transducers. Originally the material was available only in thin, 30 micron, sheets which were applicable only to low sensitivity devices. New, thicker material now available in tubular form has allowed for the design of hydrophone elements with good sensitivity and the advantages over conventional piezoceramics of flexibility, shock resistance, acoustic transparency and ease of manufacture in continuous lengths. Of specific advantage is the resistance of the material to mechanical failure due to shock. Conventional piezoceramic materials are brittle and have to be protected from tensile fracture by using compression stress rods or fiberglass wrap. These methods effectively reduce the final sensitivity of the device. Using PVF_2 eliminates the need for these protective methods and, therefore, allows for more simple and effective design. In some underwater acoustic measurements, there is a requirement that the sensor be neutrally bouyant and acoustically transparent. When using conventional piezoceramics, it is very difficult to adjust the bouyancy of a hydrophone because of the high density of the ceramic material, and impossible to design an acoustically transparent sensor. PVF_2, however, is very nearly the density of water and is essentially transparent acoustically.

Discussed in this paper is the design of a hydrophone which maximizes the advantages of the tubular PVF_2 material. The resulting design has good acoustic sensitivity (-196 dB re 1 volt per micropascal) and is resistant to the explosive shock of the equivalent of 60 pounds of TNT at 20 feet.

Glass-Ceramics: New Materials for Hydrophone Applications

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University Park, PA 16802

Single crystals of fresnoite ($Ba_2TiSi_2O_8$) and its germanium analogue ($BaTiGe_2O_8$) have been reported to have interesting piezoelectric properties. Glass-ceramics of these materials with oriented crystallites have been prepared for hydrophone applications. Samples were prepared by recrystallizing the glasses in a strong temperature gradient. Various modified compositions in the above system were tried to optimize the physical properties. These glass-ceramics showed high piezoelectric voltage coefficient g_h (100-120 x 10^{-3} Vm/N), low dielectric constant (10-15) and densities less than 4000 kg/m^3. There was no variation of g_h with pressure up to 10 MPa for all the compositions. The g_h coefficients and the product $d_h g_h$ of these glass-ceramics were comparable to PVF_2 and much higher than solid PZT.

11:15 a.m. SESSION 6A: Electro-Optics-II
Chairman: S. Kurtz

6A-1 Electrogyration and Electro-Optic Effects of Some Ferroelectric Crystals (invited) - J. Kobayashi, Waseda University, Japan

6A-2 PLZT Reflective Displays (invited) - G. Haertling, Motorola, USA

6A-3 Switching Speed Improvements in PLZT Shutters - G.R. Laguna, Sandia National Laboratories, USA

6A-4 Edge-Sealed PLZT Shutters for Operation in High Humidity/Temperature Environments - R.P. Cutler and J.O. Harris, Jr., Sandia National Laboratories, USA

6A-5 Photoferroelectric Sensitivity Enhancement in PLZT Ceramics by Thermal Diffusion of Metals - C.E. Land and P.S. Percy, Sandia National Laboratories, USA

6A-6 A Fibre Optic Electric Field Sensor Using the Electro-Optic Effect of $Bi_4Ge_3O_{12}$ - K. Shibata, Fuji Electric, Japan

ELECTROOPTICAL AND PIEZOELECTRIC EFFECTS OF SOME FERROELECTRIC CRYSTALS

By J. KOBAYASHI

Department of Applied Physics, Waseda University,

4-4-1, Okubo, Shinjuku-ku, Tokyo, Japan

The measurements of the anisotropy of optical susceptibilities, i.e., optical birefringence and activity, is one of the most important clues for studying physical properties of ferroelectric crystals. It must be stressed that the importance of the optical activity, which can sensibly respond to the modulation of the crystal lattice and to the change of the bonding nature of constituent atoms, has become appreciated in these several years. On the other hand, the electrooptic effect is utilized for various aspects of applications.

The measurement of optical activity has long been looked upon as almost unfeasible. We also claim that even the modern advanced methods for the measurement of birefringence are not satisfactory. This comment issues from the following facts. Accurate measurements of birefringence can never be made without full account for

the related optical activity, and furthermore, the orientation of optical indicatrix of a crystal belonging to the monoclinic or triclinic systems is rotated about some of their optical axes when electric fields are applied on it. So the invention of a general and accurate method for the simultaneous measurement of optical birefringence and activity of any crystals, including those belonging to monoclinic and triclinic systems is strongly requested.

We have developed a method which nearly meets the above mentioned requirements, and applied it to several problems,e.g., TGS,$PbTiO_3$,$(NH_4)_2BeF_4$ and GMO. In this paper we will summarize the results and particularly examine the utility of optical activity and electrogyration effect for the study of ferroelectrics.

ABSTRACT

PLZT REFLECTIVE DISPLAYS

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Since the first development of the transparent, ferroelectric, electrooptic PLZT ceramics in 1969, there have been continuing efforts to utilize these materials in applications such as shutters, light modulators, color filters, image storage devices and displays. The first practical device for PLZT ceramics was a military application; i.e., a nuclear flashblindness eye protection system which essentially consists of wide area, fast responding, electro-optic shutters that pass or block light on command from a photo sensor. A second application was also a shutter-type device, a high speed data recorder, consisting of a linear array of hundreds of tiny light gates driven on or off with logic circuitry. This paper will report on the first practical application of PLZT ceramics in the area of displays. Data will be presented on the operational characteristics of both seven segment and sixteen segment, reflective-type displays. Significant features include wide viewing angle, wide operating temperature range, high speed and color capability. Advantages and disadvantages will be discussed.

SWITCHING SPEED IMPROVEMENTS IN PLZT SHUTTERS

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Flashblindness Protective Devices Division

Sandia National Laboratories
Albuquerque, New Mexico 87185

ABSTRACT

Development of large diameter (up to six-inches) PLZT shutters for the USAF is an ongoing project at Sandia National Laboratories. One of the aspects in this development is to attain the same switching speeds achieved in smaller diameter devices. The effort is separated into two parts. The first part is to model the device as a linear time-invariant system thereby allowing the use of frequency analysis. The second part is to utilize the fact that the PLZT ceramic used in these shutter devices is a ferroelectric material, thus properties of the hysteresis loop can be used to advantage.

Experimental data is used to determine the impulse response of the shutter device. This response is a property of the geometry of the particular shutter. In the present work, no effort is made to predict this response; instead, the response is determined experimentally. Then, the mathematical formalism of frequency analysis is used to calculate the response of the device to various inputs. A comparison is made between the predictions and experimental results. Then, a particular input is suggested for the best switching response obtainable from this analysis.

Finally, the use of the hysteresis properties of the shutter is described. This analysis is then combined with the above to obtain improved switching response in all sizes of PLZT shutters.

EDGE-SEALED PLZT SHUTTERS FOR OPERATION IN HIGH HUMIDITY/TEMPERATURE ENVIRONMENTS

ROBERT P. CUTLER AND JAMES O. HARRIS, JR.

Sandia National Laboratories
Albuquerque, New Mexico 87185

ABSTRACT

Production of the EEU-2A/P Thermal/Flash Protective Goggle for the USAF Strategic Air Command has recently been completed. This goggle utilizes an electroded PLZT (lead lanthanum zirconate titanate) ceramic bonded between crossed polarizers in the classical Kerr cell configuration to form a bonded lens assembly (BLA).

One limitation of these goggles is that they must be stored in desiccated containers and their exposure to high temperature/high humidity enviroments must be restricted. Exposure to these environments results in nonuniform shutter transmission in both the open and closed states due to exacerbated space charge effects, and, ultimately, in bleaching of the polarizer film. An effective edge seal for the lenses would eliminate the desiccation requirement and the restriction on environmental exposure. This technology is being developed at Sandia for use on new prototype shutter devices for the U.S. Military.

The design and fabrication of the first edge-sealed BLA prototypes are described. This includes a discussion of three different glass metalization techniques, two glass-to-metal sealing methods, and two methods of making electrical connections through the hermetic seal to external connection points. Finally, data is presented showing performance differences between sealed and non-sealed BLA's following long term exposure to high temperature/high humidity environments.

PHOTOFERROELECTRIC SENSITIVITY ENHANCEMENT IN PLZT CERAMICS BY THERMAL DIFFUSION OF METALS

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ABSTRACT

We reported in previous papers that both the near-UV and visible photosensitivities of PLZT ceramic image storage and display devices can be greatly enhanced by ion implantation. We present new results which suggest that a combination of thermal diffusion of Al and implantation of Xe produces photosensitivity enhancement greater than that achieved with Xe implantation alone.

*This work performed at Sandia National Laboratories supported by the U.S. Department of Energy under contract number DE-AC04-76DP00789 and by the Army Research Office.

A Fibre Optic Electric Field Sensor Using The Electrooptic Effect Of $Bi_4Ge_3O_{12}$

K. Shibata

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An accurate fibre optic electric field sensor using the electrooptic effect of a $Bi_4Ge_3O_{12}$ crystal has been developed. Because $Bi_4Ge_3O_{12}$ has a $\bar{4}3m$ point-group symmetry, this crystal is used as the electrooptic one in this sensor.

Crystals of this point-group symmetry have no pyroelectricity, natural birefringence nor optical activity. A sensor using crystals with pyroelectricity and natural birefringence has temperature dependences. Therefore it is expected that this sensor has no temperature dependences based on these two properties and that a high accuracy sensor can be realized.

And because this crystal has also no optical activity, the sensor can be formed in transverse mode of modulation and its sensitivity can be easily adjusted with changing length of the crystal.

And the relative dielectric constant of $Bi_4Ge_3O_{12}$ is about 16 and smaller than such electrooptic crystals as $LiNbO_3$, $Bi_{12}SiO_{20}$ and $Bi_{12}GeO_{20}$. Therefore the disturbance of a measured electric field by this sensor is small.

The measured temperature dependence of this sensor is $\pm 0.5\%$ between -15 and $60^{\circ}C$. This result implies that the sensor has a very high accuracy and it is considered that the electrooptic coefficient of $Bi_4Ge_3O_{12}$ has no temperature dependence in this temperature range.

The sensor's directivity has been applied to the measurement of the strength and the direction of the electric field at a surface of a coil-end of a high voltage generator.

The numerical solution of this electric field will be obtained with a computer simulation and the measured value will be compared with the calculated one and the disturbance of the electric field by the sensor probe containing $Bi_4Ge_3O_{12}$ will be estimated.

11:15 a.m. SESSION 6B: Dielectrics (Properties)
Chairman: C. Pulvari

6B-1 Defects and Transport in $LiNbO_3$ (invited) - D. M. Smyth, Lehigh University, USA

6B-2 Effect of Substitutions in the Cationic Sites on the Electrical Conductivity and Aging of PZT Piezoelectric Transducers - L. Eyraud, P. Eyraud, J. Mathieu and B. Claudel, I.N.S.A., France

6B-3 Space-Charge-Limited Current in Thin PLZT Samples - M. Simhony, Hebrew University, Israel

6B-4 I-V and C-V Characteristics of Ferroelectric Lead Germanate on Silicon - S. B. Krupanidhi and A. Mansingh, Queen's University, Canada

6B-5 Dielectric and Electro-Optic Properties of Grain-Oriented Transparent (Pb, Ba, La)Nb_2O_6 Ceramics - K. Nagata, Y. Kawatani and K. Okazaki, National Defense Academy, Japan

6B-6 Dielectric and Pyroelectric Properties of Solid Solutions $(CH_3NHCH_2COOH)_3\ CaCl_{2(1-x)}I_{2x}$ - S. Fujimoto, N. Yasuda and A. Kawamura, Gifu University, Japan

6B-7 Dielectric Characterization of Tourmaline Single Crystal at High Temperatures in RF Region - P.V. Webb and R.K. Pandey, Texas A&M University, USA

Defects and Transport in $LiNbO_3$

D. M. Smyth
Materials Research Center
Lehigh University
Bethlehem, PA 18015

$LiNbO_3$ is an electro-optic material with properties that are convenient for a variety of applications. The effects of compositional variations on its electrical and optical properties are therefore of considerable interest. The $LiNbO_3$ phase tolerates Li_2O and oxygen deficiencies amounting to several percent at temperatures above 900°C. The resulting defect structures have been studied by means of equilibrium conductivity measurements as a function of oxygen partial pressure, temperature, and impurity additions for single crystalline samples having compositions corresponding to the Li_2O-rich and Li_2O-deficient phase boundaries and the congruently melting composition. Additional information on weight and density changes and on impurity diffusion have become available. The current status of the defect chemistry of $LiNbO_3$ and its relationship with electrical properties will be reviewed. (Supported by the Air Force Office of Scientific Research.)

EFFECT OF SUBSTITUTIONS IN THE CATIONIC SITES ON THE ELECTRICAL CONDUCTIVITY AND AGING OF PZT PIEZOELECTRIC TRANSDUCERS.

Lucien EYRAUD Paul EYRAUD Jean Claude MATHIEU Bernard CLAUDEL

I.N.S.A, France

ABSTRACT

Phenomena of conduction in an electrical field and of aging in ceramics of PZT type are the cause of important limitations to the development of some industrial applications. The presently admitted assumptions about this aging rest upon the instability of the domain configuration after polarization of the ceramic elements. The conduction mechanism is up to now not well understood.

The aim of this study is to analyze the links between these two phenomena and the structure defects, especially the cationic vacancies. It is shown that the preparation process of PZT by coprecipitation offers the possibility of getting rid of the defects, by substitution of heterovalent ions on both cationic sites, eventually with an ambivalent ion.

This preparation process which implies lower temperatures, compared to the dry process, shows that is possible to tailor solid solution compositions which cannot be obtained by the conventional method.

SPACE-CHARGE-LIMITED CURRENT IN THIN PLZT SAMPLES*

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The Racah Institute of Physics, The Hebrew University of Jerusalem,
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Currents in thin (9 and 24 μm) samples of PLZT 8/65/35 under constant applied voltages decrease with time by up to five orders of magnitude, then they may spontaneously change direction and flow for hours opposite to the applied field.[1] This is explained by changes of polarization and internal bias in the samples, and by injection of free charge (electrons or holes). When a voltage V is applied to a "virgin" sample, the injected charge causes a space-charge-limited current j_{scl},

$$j_{scl} \propto \varepsilon\mu V^2/d^3$$

(ε is the permittivity, μ is the charge mobility, and d is the sample thickness). Initially, j_{scl} is much larger than the current $j_{con} = \sigma V/d$ due to the conductivity σ of the material. With time, more and more injected carriers are trapped on various defects of the ferroelectric sample. The trapped charge builds up an electric field opposite to the applied field, reducing the current to a value below j_{con}, and changing the internal bias field of the sample. The space charge collected on domain walls may then cause domains to flip over. As a result, the internal field exceeds the applied field and the current reverses direction. Various other aspects of space-charge-limited currents and difficulties of their measurements in polar materials are discussed.

*Part of this work was carried out at the Center for Laser Studies, The University of Southern California, Los Angeles, CA 90007, under a grant (DAAG 29-77 G-0147 and 29-79-C-0111) of the U.S.Army Research Office, Durham, N.C.

[1] Ferroelectrics 29, 175 (1980).

I-V AND C-V CHARACTERISTICS OF FERROELECTRIC LEAD GERMANATE ON SILICON

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Delhi University,
Delhi - 110007, INDIA

Ferroelectric lead germanate ($Pb_5Ge_3O_{11}$) films have been deposited on silicon substrates to achieve non-volatile memory devices. Physical characterization of the films has been done in terms of structure (TEM, XRD), composition (AAS) and surface growth (SEM). The ferroelectric behaviour of the lead germanate films has been examined in terms of dielectric constant, dc conductivity and polarization hysteresis as a function of temperature. Films show a broad dielectric anamoly and a dielectric constant less than that of bulk at the transition temperature and has been attributed to the interface phenomenon.

The interface of lead germanate-silicon has been studied by noting the I-V characteristics. The I-V pattern appears analogous to that observed in semiconductor heterojunctions and suggests the formation of a n-n^+ at the interface of ferroelectric lead germanate (n) and silicon (n^+). The low voltage (1V) I-V behaviour indicates a combination of two conduction mechanisms : generation-recombination and tunnelling, as the current I obeys the relation $I = I_0 \cdot \exp\left(\frac{qV}{\eta kT}\right)$ between 0 - 0.6V and $I = I_0 \exp(AV)$ between 0.6 - 1 V. The I-V behaviour at voltages 1V observed nearly ohmic and believed to be the bulk effect.

The capacitance-voltage (C-V) measurements made at 1 MHz on MFS structure exhibit a hysteresis indicating a ferroelectric feild effect memory behaviour. The shift of the flat band voltage is consistent with the polarization direction and suggests that the device is operating in a polarization limited mode. The offset of the C-V hysteresis in the positive voltages may be attributed to the formation of heterojunction and also to the presence of immobile charges at the interface.

Dielectric and Electrooptic Properties of Grain-Oriented Transparent $(Pb,Ba,La)Nb_2O_6$ Ceramics

K. Nagata, Y. Kawatani and K. Okazaki
The National Defense Academy, Yokosuka 239, Japan

Abstract

The compositions of Ba and La substituted in the lead metaniobate, $(Pb_x,Ba_{1-x})_{1-3y/2}La_yNb_2O_6$, were hot-pressed and the dielectric, piezoelectric, optical and electrooptic properties were measured for the grain oriented samples. The anisotropies of about 1.3 to 2 times in the permittivity, electromechanical coupling factor and electrooptic coefficient were found between the parallel and perpendicular directions to the hot-pressing direction. Polished specimens in the compositional range of x=0.40-0.70 and y=0.04-0.08 showed the transmission of 50-60% at a wave-length 0.8μm (0.2mm thickness). They have shown the high electrooptic effects corresponding to PLZT. The linear and quadratic electrooptic coefficients are 3.04×10^{-10}m/V (x/y=70/2) and $2.78\times10^{-16}m^2/V^2$(60/8), respectively. Microstructures were observed for the hot-pressed samples using a scanning electron microscope and grain-orientation phenomenon of tungsten-bronze type materials will be discussed.

Dielectric and Pyroelectric Properties of Solid Solutions$(CH_3NHCH_2COOH)_3 \cdot CaCl_{2(1-x)}I_{2x}$

Sanji Fujimoto, Naohiko Yasuda and Akira Kawamura;Department of Electrical Engineering, Gifu University, Yanagido, Gifu, Japan
Tadashi Hashiya; Takayama Junior College, Takayama, Japan

Much attention has been given to triscarcosine calcium chloride(TSCC)[1]. Dielectric and pyroelectric properties of $(CH_3NHCH_2COOH)_3 \cdot CaCl_{2(1-x)}I_{2x}$(TSCCI) were measured under pressures. We have presented the dielectric properties of TSCCB[2]. We noted that its dielectric hysteresis loop is partially or completely displaced along the field axis, i.e. shows a permanent self bias. The asymmetry in the hysteresis loop should be explained on the basis of an internal field which arises because of Br incorporated into lattice. The larger internal bias field is induced in TSCC by the partial substitution of I for Cl than that of Br(~50kV/cm for I and ~5kV/cm for Br).The internal bias field Eb varies with temperature T, pressure and concentrations of I or Br. The maximum permittivity ε_{max} is depressed and the dielectric loss is reduced by the large internal field. Such large internal field is known to lead to the prediction of high performance pyroelectric detector. For TSCC, the pyroelectric charge P increases continuously below the Curie point T_c and tends to saturate with T. For TSCCI, the pyroelectric charge increases near T_c, exhibits a maximum and then decreases with T. Such behavior is associated with the variation of Eb with T. It is noted from this temperature dependence of P that the pyroelectric coefficient(dP/dT) or dP/EdT is almost constant in the temperature range of ~20°C, whereas that of TGS varies greatly with T.

1.S-IMF;Ferroelectrics 37 (1981).
2.S.Fujimoto et al, J.Phys.D15 487 (1982).

DIELECTRIC CHARACTERIZATION OF TOURMALINE SINGLE CRYSTAL AT HIGH TEMPERATURES IN RF REGION

P.V. Webb and R.K. Pandey
Electrical Engineering Department
Texas A&M University
College Station, TX 77843

Tourmaline is a complex silicate of boron and aluminum containing various other metals, $R_6Al_3B_2(OH)_2Si_4O_{19}$, where R is iron, magnesium, and the alkalies. It occurs in single crystalline form as various natural gems, which differ in color depending on their content of iron, magnesium, or alkalies. The pyroelectric effect in tourmaline has been known as early as 1856 and it exhibits interesting piezoelectric properties. These characteristics of tourmaline have made it useful for infra-red detectors; surface acoustic wave (SAW), optical, and other microwave devices.

The temperature dependence of pyroelectric current (I_{pyr}), real (ε_r') and imaginary (ε_r'') permittivity, and electrical resistance (ρ) of tourmaline will be discussed between room temperature and 700°C. The effect of frequency between 0 and 13 MHz and temperature on these parameters will also be presented. The literature is full of contradictions so far as the temperature and frequency dependence of I_{pyr}, ε_r', ε_r'', and ρ are concerned. We hope that our investigations will fill this void and would be beneficial to the scientific and technological communities. Our investigations will include various types of tourmaline crystals found in nature. Details of the instruments employed in these investigations will also be emphasized.

8:45 a.m. SESSION 7A: Integrated Optics
Chairman: A.M. Glass

7A-1 Electro-Optic Materials for Optical Communications (invited) - R. Sundahl, Bell Laboratories, USA

7A-2 Integrated Optics Applications for Ferroelectric Materials (invited) - H.F. Taylor, Naval Research Laboratory, USA

7A-3 Infrared Holographic Gratings in $LiNbO_3$ Optical Waveguides by a Two-Step Process - V. Wood and R.C. Sherman, Battelle Columbus Laboratories, USA

7A-4 $LiNbO_3$ Guided-Wave Interferometric Modulators - F. J. Leonberger, Massachusetts Institute of Technology, USA

7A-5 Proton Exchange in $LiNbO_3$ - J.L. Jackel, C.E. Rice and J.J. Veselka, Jr., Bell Laboratories, USA

7A-6 Damage Resistant $LiNbO_3$ for High Power Modulators and Switches - G.E. Peterson, B.I. Greene, S.D. Poulsen, J. Jackel and A.M. Glass, Bell Laboratories, USA

7A-7 Lithium Niobate Waveguides and Their Susceptibility to Optical Damage - R.L. Holman, Battelle Columbus Laboratories and P.J. Cressman, University of Rochester, USA

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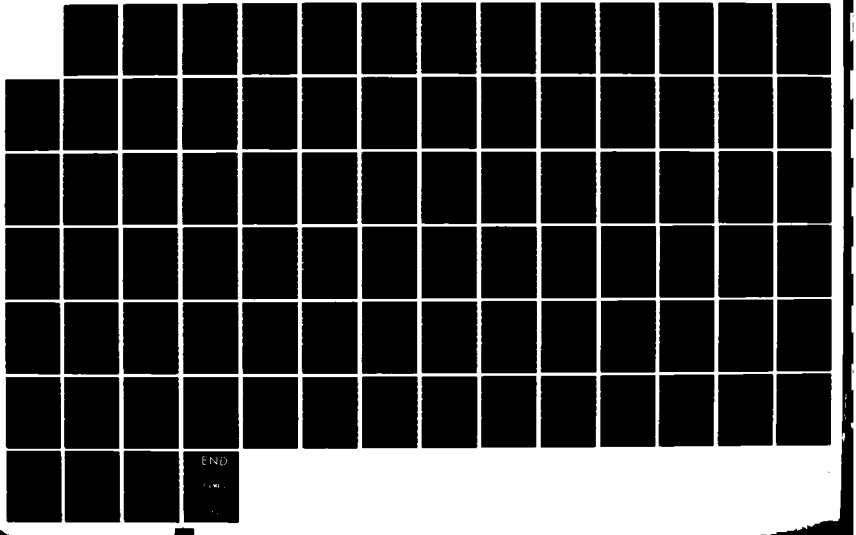

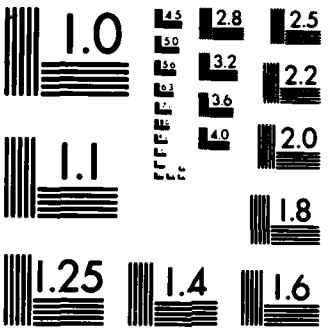

MICROCOPY RESOLUTION TEST CHART
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INTEGRATED OPTICS APPLICATIONS FOR FERROELECTRIC MATERIALS

Henry F. Taylor
Naval Research Laboratory
Washington, DC 20375

Abstract

Lithium niobate is presently the most commonly used material for integrated optics because of such favorable properties as low acoustic and optical attenuation, large electrooptic coefficient, and high resistivity. Current research is oriented mostly towards applications in signal processing (rf spectrum analyzers, correlators, high-speed A/D converters), and communications (wideband modulators, switches, multiplexing devices). Recent progress in integrated optical device work at a number of laboratories will be reviewed, and future prospects for lithium niobate and other ferroelectric materials discussed.

Electro-Optic Materials for Optical Communications (invited)-
R. Sundahl, Bell Telephone Laboratories

(No Abstract)

INFRARED HOLOGRAPHIC GRATINGS IN $LiNbO_3$ OPTICAL WAVEGUIDES BY A TWO-STEP PROCESS

Van E. Wood and Rand C. Sherman
Columbus Laboratories, Battelle Memorial Institute
505 King Avenue, Columbus OH 43201

There is considerable interest in integrated optical devices for use with fiber-optic systems and solid-state light sources operating in the near-infrared range. One useful element in such devices is the thick phase diffraction grating, which can be used as a beam splitter, as a demultiplexer, or as a wide-angle switch. Such gratings are best formed using guided beams at the wavelength of interest in order to reduce problems arising from inhomogeneous wavefronts. It is difficult to form such gratings using infrared wavelengths in most optical waveguide materials since the materials have relatively large optical band gaps.

We have found that gratings of diffraction efficiency up to 25% can be formed in single-mode Ti-indiffused $LiNbO_3$ waveguides by intersecting 1.06 μm wavelength beams provided the guide is "sensitized" by passing a broad beam of moderately high intensity red light (0.633 μm) through it prior to introducing the infrared beams. These gratings are stable in the dark for at least 24 hours. Exposure to a total guided-wave energy of red light of no more than 12 μjoules is sufficient for sensitization. The infrared power entering the waveguide is typically about 1 mW. A two-photon, two-step process is suggested. TE polarization is used for both sensitizing and recording beams. The gratings can be erased by exposure to another broad beam of guided visible light. The gratings are approximately 200 μm in width and the grating spacing is about 4 μm.

Holographic gratings can also be written, at much higher powers, using the 1.06 μm beams alone. The recording sensitivity in this case is independent of intensity, suggesting a two-step process in which one step is readily saturated. At the power levels required to form the gratings using infrared beams alone, damage to or destruction of the waveguide is not infrequent.

The relation of these observations to similar effects seen in bulk sillenite crystals, to the "infrared enhancement" effect noted in two-photon one-step recording in bulk $LiNbO_3$, and to the changes found in switching characteristics of $LiNbO_3$ channel-waveguide infrared directional couplers after similar sensitization with a visible beam will be discussed.

This work has been supported in part by the U. S. Army Research Office.

$LiNbO_3$ Guided-Wave Interferometric Modulators

F. J. Leonberger
Lincoln Laboratory, Massachusetts Institute of Technology
Lexington, Massachusetts 02173

Abstract

The characteristics and applications of $LiNbO_3$ interferometric modulators are reviewed. These devices, which are under development at a number of laboratories, are single-mode waveguide versions of Mach-Zehnder interferometers. Waveguide Y-branching circuits serve as optical power splitters and combiners. The output intensity of the modulator is controlled by varying the relative phase of the light in the two interferometer arms. This phase control is in most cases done electrooptically. The single-mode waveguides, which typically have a cross section of 3 x 5 μm, are formed by Ti indiffusion.

These modulators have been studied individually and optical circuits which contain modulator arrays have been used for a number of applications. Discrete electrooptic modulators have been built which have a 26-dB extinction ratio, 1-V extinction voltage (V_π) and 500-MHz bandwidth. Traveling-wave devices have been reported with up to 18-GHz bandwidth. The modulators can be operated in a linear light-output vs voltage mode and as such have been used for electomagnetic field detection. Optical circuits containing modulator arrays are under development for high-speed analog-to-digital conversion, picosecond sampling and optical logic, frequency modulation and optical temperature sensing. Electrooptic A/D converters have been demonstrated for the 4-bit 828-Megasample/s (MS/s) and 2-bit 1000-MS/s range. The picosecond electrooptic sampler is designed to slice out picosecond-wide pulses from a continuous amplitude varying optical signal. Special interferometers driven by high-power psec-wide laser pulses offer the possibility of building fast all-optical exclusive-or (XOR) gates. Interferometric circuits have also been used to efficiently generate GHz single-sideband suppressed carrier modulation. For temperature sensing applications, an interferometer with unequal arm lengths has been fabricated. In this all-optical sensor, temperature variations produce intensity modulation. Experimental results suggest that an operating range of 700°C and a resolution of 2×10^{-3}°C should be possible.

Proton Exchange in $LiNbO_3$

J. L. Jackel, C. E. Rice, J. J. Veselka, Jr.

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Holmdel, NJ 07733

This talk will review our current work on proton exchange in $LiNbO_3$. Proton exchange, which takes place when the $LiNbO_3$ substrate is immersed in an appropriate proton source, produces high index changes: $\Delta n_e \cong 0.12$, with an index profile which approximates a step-function, and $\Delta n_o \cong -0.05$. We will concentrate here on the exchange media we have found most useful, melts of benzoic acid, or benzoic acid with small additions of alkali metal salts. We will discuss diffusion kinetics, index profiles, waveguide patterning, and loss measurements.

The extremely large increase of the extraordinary refractive index obtained using proton exchange allows waveguide components to be made smaller than is possible with standard diffusion techniques. Two other aspects of proton exchange promise future usefulness. First, because the process takes place at low temperatures, i.e. 100 - 250 ^{o}C, exchange can be performed after titanium diffusion with no effect on the diffused waveguides. It can therefore be used to form additional (high index change)structures in the same region as the titanium diffused guides, and thus expand the range of possible devices. Examples to be discussed include gratings, and polarization separators. Second, proton exchange greatly diminishes optical damage, both in virgin and in previously titanium diffused $LiNbO_3$. This makes possible the use of higher powers, particularly for visible light. We will describe some of the optical damage measurements in detail.

Damage Resistant $LiNbO_3$ for High Power Modulators and Switches

by

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Murray Hill, N.J. 07974

and
J. Jackel and A. M. Glass

Bell Laboratories,
Crawfords Corner Road
Holmdel, N.J. 07733

ABSTRACT

Titanium diffusion into $LiNbO_3$ is the most commonly used technique for the fabrication of optical waveguides for hybrid integrated optical devices. Both ordinary and extraordinary waves can be guided and fabrication of complex guided wave structures is relatively straightforward. However, Ti diffused guides suffer from a high photorefractive sensitivity ("optical damage") which makes them of limited use for application in the visible spectrum.

For certain device applications we wished to switch, gate and modulate a high power, mode locked, ring dye laser which operates at 620 nm. This laser has a repetition rate of 110 MHz, a pulse width of 0.2 psec and an average power of 20 mW. When focused into a planar waveguide using a 30 cm lens and a prism coupler the average optical intensity inside the guide is about $5kw/cm^2$ and the peak pulse intensity is about $5x10^8$ w/cm^2. A titanium diffused $LiNbO_3$ optical wave guide will not operate under these conditions for more than a few seconds. It was recently shown that the introduction of hydrogen into a $LiNbO_3$ waveguide during Ti diffusion at 900 to 1100 degrees reduces the photorefractive sensitivity by about two orders of magnitude. It has also been found that large concentrations of hydrogen can be exchanged for Li ions by immersion of $LiNbO_3$ in low temperature proton sources such as acids or hydrate melts. Proton exchange results in waveguides having very large increases of the extraordinary index. Because of the low temperature required for this latter process, fabrication of integrated devices are readily made simply by masking the surface during exchange.

A number of modulators, switches and gates have been constructed using proton exchange and rather elementary masking methods. We find that they operate satisfactorily with the ring laser previously mentioned.

LITHIUM NIOBATE WAVEGUIDES AND THEIR SUSCEPTIBILITY TO OPTICAL DAMAGE

by

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Battelle's Columbus Laboratories
505 King Avenue
Columbus, Ohio

and

Paul J. Cressman
Institute of Optics
University of Rochester
Rochester, New York

The laser-induced photorefractive effect, also known as optical damage, causes time-varying refractive index distortions to occur in lithium niobate waveguiding layers. The optical manifestation of this effect (assymmetric in-plane spatial changes in the waveguide's optical output) has been shown to depend on the laser power density, the laser wavelength, the laser polarization, the crystallographic direction of propagation, the exposure time, and critically on the chemical processing conditions under which the waveguide was formed. Previous studies have contrasted the long-term optical performance of lithium niobate waveguides formed principally by the out-diffusion of lithium oxide and by the in-diffusion of titanium ions. Waveguides formed under oxidizing conditions and in the presence of water vapor have shown superior laser-power-handling performance. Out-diffused waveguides were found to offer 20-30 times greater laser-power-handling performance than in-diffused waveguides at 632.8 nm. More recently, however, there has been considerable interest in lithium niobate waveguides formed by a new lower-temperature process: proton exchange in benzoic acid. It has been reported that proton-exchanged waveguides possess a large and sharp extraordinary refractive index profile created by the surface exchange of lithium with hydrogen. This proton-exchange process has also been applied to modify the refractive index profile of conventional titanium-in-diffused waveguides. Yet, the long-term optical performance of these waveguides has not been explored. Accordingly, it is the purpose of this study to quantify the laser-power-handling characteristics of proton-exchange lithium niobate waveguides, and to compare their performance with that of in- and out-diffused lithium niobate waveguides formed at higher temperature.

8:45 a.m. SESSION 7B: Electrostriction
Chairman: J. Dougherty

7B-1 Electrostriction (invited) - L.E. Cross, The Pennsylvania State University, USA

7B-2 Internally Electroded Piezoelectric Ceramic Actuator (invited) - M. Yonezawa and S. Takahashi, Nippon Electric, Japan

7B-3 Electrostriction in PZT-Family Antiferroelectrics - K. Uchino and S. Nomura, Tokyo Institute of Technology, Japan

7B-4 Recent Applications of PMN-Based Electrostrictors - S. Nomura and K. Uchino, Tokyo Institute of Technology, Japan

7B-5 The Effects of Various B-site Modifications on the Dielectric and Electrostrictive Properties of Lead Magnesium Niobate Ceramics - D.J. Voss, S.L. Swartz and T.R. Shrout, The Pennsylvania State University,USA

7B-6 Electrostriction and Its Relationship to Other Properties in Perovskite-Type Crystals - K. Rittenmyer, A.S. Bhalla, Z.P. Chang and L.E. Cross, The Pennsylvania State University, USA

7B-7 Direct Measurement of Electrostriction in Perovskite Type Ferroelectrics - M. Shishineh, C. Sundius, T. Shrout, L. E. Cross, The Pennsylvania State University, USA

Electrostriction

L.E. Cross

Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16802

Electrostriction is the basic electromechanical coupling in all centric crystals and glasses, and the origin of the strong piezoelectric effects in all poled ferroelectric perovskite ceramics, yet reliable values of electrostriction constants are only available for a few crystals, the true temperature dependence of the constants is largely unknown, and a convincing atomistic theory for their origin has not been given.

This talk will focus upon electrostriction in oxygen octahedron type crystals where strain levels of practical interest can be achieved at realizable fields. The special features of behavior in a wide range of relaxor ferroelectric systems will be compared and contrasted with the response in simple ordered structures.

The separation of intrinsic, polarization biased electrostriction and extrinsic domain related phenomena will be considered in the piezoelectric effects in PZT, PLZT and other perovskites of complex composition.

Higher order electrostriction will be briefly touched upon and its possible effects upon elastic behavior considered.

INTERNALLY ELECTRODED PIEZOELECTRIC CERAMIC ACTUATOR

S. TAKAHASHI, A. OCHI, M. YONEZAWA, T. YANO*, T. HAMATSUKI** and I. FUKUI*
Fundamental Res. Labs., *Transmission Div., and **Overseas Transmission Div.,
NEC Corporation
4-1-1, Miyazaki, Miyamae-ku, Kawasaki, 213 Japan
*,**1753, Shimonumabe, Nakahara-ku, Kawasaki, 211 Japan

An actuator fabricated from stacks of piezoelectric ceramic plates bonded together with an adhesive or spring loaded in one of several fashions generates great strain and large force by applying an electric force. These responses to the applied force are very quick. This kind of actuator, however, has relatively large size and is unsuitable for mass production. Besides, it requires high driving voltage. If these defects are overcome, it is expected that applictions of the actuator will make great strides.

The present work describes an attempt to overcome these problems by applying to piezoelectric ceramics an internal electroding technique commonly employed in the multilayer cermic capacitor industry. According to the technique, the opposite electrode gap can be short to the extent of over 10 μm. Therefore, it becomes possible to be driven by applying a relatively low voltage. Typical properties for an actuator made on an experimental basis (9 mm long, 6 mm^2 cross section and 230 μm internal electrode gap) are as follows:

(1) Displacement 7.8 μm/230 V
(2) Strain 8.7×10^{-4}/230 V
(3) Force 200 N/200 V (3.4×10^7 Nm^{-2}/200 V)
(4) Response 100 μs
(5) Capacitance 34 nF
(6) Longitudinal elastic modulus 4×10^{10} N/m^2
(7) Bending strength 6.5×10^7 N/m^2

ELECTROSTRICTION IN PZT-FAMILY ANTIFERROELECTRICS

Kenji UCHINO and Shoichiro NOMURA

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Ookayama, Meguro-ku, Tokyo 152, JAPAN.

Abstract

In our recent paper a phenomenological theory of electrostriction has been proposed in antiferroelectrics.[1] The electrostrictive terms have been introduced in Kittel's free energy expression as follows:

$$G_1 = \frac{1}{4}\alpha(T)(P_a^2+P_b^2) + \frac{1}{8}\beta(P_a^4+P_b^4) + \frac{1}{12}\gamma(P_a^6+P_b^6) + \frac{1}{2}\eta P_a P_b - \frac{1}{2}\chi_T P^2 + \frac{1}{2}Q(P_a^2+P_b^2+2\Omega P_a P_b)P \quad (1)$$

where P_a and P_b denote the two-sublattice polarizations, χ_T the compressibility, Q and Ω are the electrostrictive coefficients.

In order to verify this expression, one of the PZT-family ceramics $Pb_{0.99}Nb_{0.02}[(Zr_{0.6}Sn_{0.4})_{0.94}Ti_{0.06}]_{0.98}O_3$ (abbreviated as PZSN) has been investigated experimentally in this work with respect to field-induced strain, dielectric constant and polarization. PZSN is in an antiferroelectric phase at room temperature and reveals an antiferroelectric to ferroelectric phase transition induced by an electric field applied (E_{tr}= 2.5 kV/mm). Large elastic strain $\Delta L/L$ of about 10^{-3} associated with the induced phase transition may be promising for a new displacement transducer. So-called "inverse" hysteresis in the strain curve is observed in a temperature range between -70°C and 0°C, which can also be used as a shape memory device. The phase diagram in the electric field - temperature plane, the lattice parameter changes associated with the field induced transition, and the magnitude of the spontaneous or induced piezoelectric constant can be explained consistently in terms of the electrostrictive coefficients Q and Ω in our extended phenomenology.

In addition, frequency dependence of the induced strain which can follow up to 5 Hz at room temperature is discussed generally on the basis of a dynamical phenomenological theory.

1) K.Uchino,L.E.Cross,R.E.Newnham and S.Nomura: J.Appl.Phys.52 (1981)1455.

Recent Applications of PMN-Based Electrostrictors

Shoichiro NOMURA and Kenji UCHINO

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Ookayama, Meguro-ku, Tokyo 152, JAPAN.

Abstract

$Pb(Mg_{1/3}Nb_{2/3})O_3$ (abb. PMN) -based ceramics reveal a superior electrostrictive response in hysteresis and aging effect as well as in its magnitude, in comparison with the piezostriction of the PZT family. In this paper some of recent applications of the PMN-based electrostrictor are reviewed, including optical control (sensitive AC interferometer, bistable optical device and deformable mirror) and mechanical control devices (hob microdisplacement actuator and oil-pressure control servo-valve).

The sensitivity of an AC interferometric dilatometer has been improved remarkably up to $\Delta L/L \sim 10^{-13}$ by using a DC mechanical servo of the electrostrictor which can compensate the light pathlength fluctuation due to the slow thermal dilatometric change or the mechanical vibrational noise.

A combination of the Fabry-Perot optical resonator and the displacive actuator results in a simple bistable optical device (BOD). The feedback is set by applying the voltage proportional to the output light intensity onto the PMN pusher. Stabilization of the light intensity less than 1/150 of the incident intensity fluctuation has been achieved with this BOD device.

The unimorph-type deformable mirror of an aluminized glass attached on the PMN plate has been prepared for adaptive optical control. The base plate consists of three thin ceramic films stacked together, each of which has a different electrode configuration for functioning as refocusing or coma aberration.

A multilayered-PMN actuator can also compensate the positional error of a cutting tool such as a hob machine. Reproducible mechanical driving under very high stresses is essential in this case.

Highly-responsive oil pressure control up to 1 kHz has been attained with a servo-valve flapper of a PMN:phosphor bronze bimorph type. The voltage proportional to the displacement of the spur-rod is fed back to the bimorph through an amplifier, resulting in real-time precise control of oil pressure.

The Effects of Various B-site Modifications on the Dielectric and Electrostrictive Properties of Lead Magnesium Niobate Ceramics

D.J. Voss, S.L. Swartz and T.R. Shrout

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Abstract

The perovskite relaxor ferroelectric lead magnesium niobate ($PbMg_{1/3}Nb_{2/3}O_3$, hereafter designated PMN) was first synthesized in the late 1950's and has since been widely investigated for both dielectric and electrostrictive strain applications. The dielectric properties of PMN are characterized by a broad, frequency dependent maximum of the dielectric constant just below room temperature. The magnitude of this maximum (at 1 KHz, ~15,000 for ceramic PMN) decreases and the temperature of this maximum increases with increasing frequency. Due to the large dielectric constant of PMN, electrostrictive strains are comparable to the piezoelectric strains of PZT ceramics[1].

Recent publications, out of this laboratory, have described an improved fabrication technique for ceramic PMN[2], and demonstrated that the dielectric properties of PMN are quite dependent on fabrication parameters (stoichiometry, sintering temperature, etc.)[3]. The purpose of this investigation is to study the effects of various B-site substitutions (Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, Ti^{4+}, Ta^{5+}, W^{6+}, etc.) and fabrication parameters on the dielectric and electrostrictive properties of PMN. The effects of substitutional cation size and valence on the maximum dielectric constant, transition temperature range, and diffuseness of transition will be determined and correlated with electrostrictive measurements.

1. S. Nomura and K. Uchino, Ferroelectrics 41, 117-132 (1982).
2. S.L. Swartz and T.R. Shrout, Mat. Res. Bull. 17, 1245-1250 (1982)
3. S.L. Swartz, T.R. Shrout, W.A. Schulze and L.E. Cross, submitted for publication.

Electrostriction and Its Relationship to Other Properties in Perovskite-Type Crystals

K. Rittenmyer, A.S. Bhalla, Z.P. Chang and L.E. Cross

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Electrostriction is the basic electromechanical coupling effect present in all solids. The direct quadratic electrostrictive effect represented in tensor notation by the coefficient, Q_{ijkl}, relates the strain induced in a solid, (ε_{ij}), to the square of the polarization, $(P_k P_l)$, in the equation,

$$\varepsilon_{ij} = Q_{ijkl} P_k P_l \tag{1}$$

Sixth and higher order terms can be added to this equation if the strain versus polarization-squared relationship is not linear. Alternatively, the electrostriction coefficients can be obtained through the converse electrostrictive effect,

$$\Delta\chi_{ij} = 2Q_{ijkl}\sigma_{kl} \tag{2}$$

by measuring the change in inverse dielectric susceptibility, $\Delta\chi_{ij}$, produced by the application of a stress, σ_{kl}. Again, higher order terms can be added phenomenologically to account for nonlinear behavior. A sixth-order term is adequate for our case. The complete converse effect can then be written as

$$\Delta\chi_{ij} = 2Q_{ijkl}\sigma_{kl} + 2\Phi_{ijklmn}\sigma_{kl}\sigma_{mn} \tag{3}$$

where Φ_{ijklmn} is a sixth order electrostriction constant. We have performed experiments of this type on several fluoride perovskite single crystals (e.g., $KMgF_3$, $KMnF_3$, $KZnF_3$, $KCaF_3$, etc.) and have evaluated both fourth and sixth order electrostriction coefficients.

The dielectric constant, which is inversely proprotional to the inverse dielectric susceptibility, is related to the amplitude and frequency of optical phonons at long wavelengths. The pressure as well as temperature dependence of this vibrational mode gives information on the anharmonicity present in the crystals lattice. It is therefore possible, as shown by Uchino[1], to relate these effects to each other and other similar anharmonic effects such as thermal expansion and higher order elastic constants, and to other properties such as compressibility and dielectric constant. These observations are discussed with respect to our measurements on the fluoride perovskites.

[1]K. Uchino, L.E. Cross, Jpn. J. Appl. Phys.

Direct Measurement of Electrostriction in Perovskite Type Ferroelectrics

M. Shishineh, C. Sundius, T. Shrout and L.E. Cross

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A simplified AC capacitance dilatometer based on the design of Uchino and Cross[1] has been constructed to measure directly the temperature dependence of electrostrictive strain in perovskite type ferroelectric crystals and ceramics. A mechanical bridge circuit is used to compensate for thermal expansion of the mechanical components eliminating the need for DC servo stabilization. The instrument has been used in the temperature range from 20°C to 200°C. In the AC method, the electrostrictive strain under AC driving field is compared to the known strain induced in a quartz reference crystal under phase locked conditions. The method has been checked with the known piezoelectric behavior of quartz and of selected PZT disk samples. Measurements of Q constants will be reported for lead magnesium niobate (PMN), lead magnesium niobate:lead titanate solid solutions (PMN:PT), lead iron niobate:lead iron tungstate (PFN:PFW) and related relaxor ferroelectrics. Temperature dependence of the electrostrictive Q constants in single crystals $BaTiO_3$ in the paraelectric phase above T_c will be reported and the results discussed and compared to earlier studies[2,3].

1. K. Uchino, L.E. Cross, Ferroelectrics 27, 35 (1980).
2. H. Beige, G. Schmidt, Exp. Technix. der Phys. 22, 393 (1974).
3. E. Huibregtse, W.H. Bessey and M.E. Drougard, J. Appl. Phys. 30, 899 (1959).

11:15 a.m. SESSION 8A: Dielectrics (Transitions and Devices)
Chairman: I. Lefkowitz

8A-1 Curie Transitions in Copolymers of Vinylidene Fluoride (invited) - J. Lovinger, Bell Laboratories, USA

8A-2 The Ferroic Phase Transition Behavior of $Pb(Zr_{0.6}Ti_{0.4})O_3$- A. Amin, Texas Instruments and L.E. Cross, The Pennsylvania University, USA

8A-3 Ferrobielastic Switching in Quartz at High Temperatures- S.M. Shiau, T.L. Anderson, R.E. Newnham and L.E. Cross, The Pennsylvania State University, USA

8A-4 Interaction of Acoustic Waves and Ferroelastic Domain Walls - S.W. Meeks, P. Maccagno and B.A. Auld, Stanford University, USA

8A-5 A New Absolute Radiometer - L. Novak and V. Dvorak, Czechoslovakia Academy of Science, Czechoslovakia

8A-6 Quantum-Ferroelectric Pressure Sensor - C.F. Clark and W.N. Lawless, CeramPhysics and S.L. Swartz, The Pennsylvania State University, USA

8A-7 I-V and C-V Characteristics of Ferroelectric SbSI(film) - Si - Metal Devices - A. Mansingh and T.S. Rao, University of Delhi, India

CURIE TRANSITIONS IN COPOLYMERS OF VINYLIDENE FLUORIDE

by

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ABSTRACT

A series of random copolymers of vinylidene fluoride and trifluoroethylene containing 52, 65, 73 and 78 mol% VF_2 have been examined by X-ray and dielectric techniques and found to undergo Curie transitions. In their ferroelectric phase, these copolymers assume structures analogous to that of the piezoelectric β-phase of PVF_2 (i.e. trans conformation and pseudo-hexagonal molecular packing; their Curie transitions extend over wide temperature ranges (∿30°C) and involve introduction of gauche$^{\pm}$ bonds leading to partly disordered chains that are packed in an expanded pseudo-hexagonal lattice. These transitions exhibit thermal hysteresis in that the ferroelectric → paraelectric transformation occurs at higher temperatures than the reverse. Poled specimens have higher Curie temperatures than their unpoled counterparts; in the 78 mol% VF_2 copolymer this causes the Curie transition to occur in unpoled specimens but to be thwarted by the onset of melting in poled films. This suggests that the absence of a distinct Curie transition in β-PVF_2 may be a result of the prior occurrence of melting. Based on this assumption, the Curie temperature of these copolymers may be extrapolated to yield an expected transition for 100% PVF_2 in the vicinity of 205°C, which is indeed ∿20°C above the experimentally observed melting point for β-PVF_2; however, if such a transition exists and if it extends over as wide a temperature as in the copolymers, its earliest crystallographic manifestations may in fact accompany the melting process.

The Ferroic Phase Transition Behavior of $Pb(Zr_{0.6}Ti_{0.4})O_3$

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Recent low temperature neutron diffraction and diffuse neutron scattering experiments on $Pb(Zr_{0.6}Ti_{0.4})O_3$ [1] revealed some interesting and unusual features: (i) the rhombohedral (R3c) rhombohedral (R3m) phase transition is rather broad, and the transition temperature is not well defined (somewhere between 250 and 300 K) as deteremined from the temperature dependence of the strongest pseudocubic 311 reflection.

(ii) The diffuse neturon scattering data show some structure in the Q range 0.9 - 3.0 A^{0-1} ($Q = \frac{4\pi \sin\theta}{\lambda}$). This type of background modulation most likely arises from static displacements in preferred directions since random displacements would simply lead to a monotonically increasing background, as is characteristic of thermal diffuse scattering. These may reflect a short range order which is a precursor of the tetragonal phase or perhaps a tendency towards ordering of Zr and Ti atoms.

The Landau-Ginzburg-Devonshire phenomenological theory for simple proper ferroelectrics has been successfully applied to the $PbZrO_3$-$PbTiO_3$ (PZT) solid solution system. The theory correctly predicts the relative stability points of the different phases in the solid state portion of PZT phase diagram. It also permits the calculation of the observed physical properties (e.g., dielectric, piezoelectric, and other coupling coefficients) as function of temperature, pressure, and applied electric fields over the entire range of single cell compositions.

We have calculated the temperature dependence of the free energy function G for the rhombohedral (R3m), tetragonal (P4mm) and orthorhombic Bmm2) modification of the prototypic (Pm3m) symmetry of $(Pb_{0.6}Ti_{0.4})O_3$ using the $PbZrO_3$-$PbTiO_3$ phenomenological theory. In this work we will present our results and correlate the neutron scattering results and those obtained from phenomenological theory.

1. A. Amin, R.E. Newnham, L.E. Cross and D.E. Cox, J. Solid State Chemistry 37, 248 (1981).

Ferrobielastic Switching in Quartz at High Temperatures

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Abstract

Quartz is ferrobielastic with Dauphiné twins differing in the orientation of the elastic compliance and piezoelectric tensor. Therefore a suitably-oriented stress can produce different strain in the two domains, causing a free energy difference between the two domain states and producing a driving force for domain reorientation and twin wall motion.

Ferrobielastic twinning has been studied optically utilizing the photoelastic effect from room temperature up to 400°C. The coercive stress for ferrobielastic switching decrease with increasing temperature. The coercive stress needed to cause switchover in synthetic crystals is about 7×10^8 Pa at room temperature. Experiments at 150°C show switchover at 5.2×10^8 Pa and at 200°C about 1.9×10^8 Pa. The coercive stress data decrease monotonically with increasing temperature up to 250°C, above which the domain patterns depart radically from those observed at lower temperatures. The inverse relationship between coercive stress and temperature continued at higher temperature but with a discontinuity at 250°C separating two apparently linear segments.

Beyond 400°C even very small stresses are sufficient to induce twinning and it becomes difficult to observe optically, therefore the electrical method is used to study twinning at near the $\alpha - \beta$ transition. Additional details concerning high temperature twinning will be presented at the meeting.

INTERACTION OF ACOUSTIC WAVES AND FERROELASTIC DOMAIN WALLS

by

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A method of injecting arrays of domain walls into the ferroelastic crystals GMO and NPP is described. The technique consists of applying an array of regularly spaced shear forces directed in such a way that alternate shear couples favor different switching directions. This technique has allowed the injection of as many as 10-30 domains in a parallepiped crystal of NPP with dimensions in the range of 1-2 cm and in thin rod-like samples. A method of controlling the spacing of the domain walls is also presented. This method consists of applying a force parallel to the plane of the wall at the position of a domain wall and then moving the force along the outside of the crystal. The domain wall will follow the external force. Using this technique domain walls have been spaced as close as a few tenths of a millimeter. Similar experiments have been performed on GMO. Measurements of the forces required will be reported. Acoustic shear waves in the frequency range of several MHz have been injected into these multidomain crystals for the purpose of studying linear and nonlinear wave-domain interactions. Results will be presented showing the filtering action of linear acoustic transmission through a ferroelastic crystal with a regular array of domains. This effect is due to constructive and destructive interference of acoustic waves reflecting from the domain boundaries. The influence of the acoustic wave on domain wall motion will also be discussed. The device implications of these experiments are discussed.

A NEW ABSOLUTE RADIOMETER

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The latent heat L of a first-order phase transition (PT) (e.g. solid-liquid transition, some structural phase transitions) provides an absolute measure of the energy; therefore a material exhibiting a PT and absorbing radiation could be used as a sensitive element (SE) of an absolute radiometer. Absorbed radiation flux P_s converted into the heat could be determined absolutely by measuring the time interval τ needed for supplying the L into the SE. τ is a known function of P_s, of the controlled heat flux W_{op} due to operating conditions (e.g. joule heating by electric current), of the exchange heat flux P_b between the SE and surroundings, and of L. The quantities P_b and L are charakteristic parameters of the radiometer and can be determined by measuring τ at $P_s = 0$ and at two different definite values of W_{op}. Suitably changing W_{op} the temperature of the SE can be increased above or decreased below the PT temperature T_{tr} so that the SE is periodically going through the PT. The proposed radiometer could be classified as a true isothermal radiometer in the sense that its response τ is measured at constant temperature T_{tr} of the SE. The beginning and the end of τ could be identified by measuring such properties (e.g. electrical conductivity, specific volume) of the SE which are considerably different in both phases or by detecting its temperature deviation from T_{tr} e.g. by means of a pyroelectric detector. Basic characteristics of an ideal isothermal radiometer are discussed and compared with those of classical thermal detectors.

Quantum - Ferroelectric Pressure Sensor

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ABSTRACT

Quantum ferroelectrics are characterized by a temperature-independent dielectric constant at low temperatures ($\partial\varepsilon/\partial T=0$), yet in this temperature range the Clausius-Mossotti relation requires that the dielectric constant have a non-zero pressure dependence ($\partial\varepsilon/\partial p\neq 0$). Consequently, a quantum ferroelectric can be used as a cryogenic pressure sensor which is independent of temperature and intense magentic fields and would be useful as a solid-state device for sensing over-pressures in superconducting magnets. Research in the ceramic system $(Cd_{1-x}Pb_x)_2\ (Nb_{1-y}Ta_y)_2\ O_7$ has revealed a compositional range where quantum effects dominate below 15K (i.e., $\partial\varepsilon/\partial T=0$). A sensor made from these ceramics will have $\varepsilon^{-1} \propto p$ up to 30 kbar, and such sensors can be made in the form of small (e.g., 2x2x5 mm) multilayer capacitors. Such devices are anticipated to have pressure sensitivities $\Delta C/\Delta p \cong 600$ pF/kbar at 4.2K.

I-V AND C-V CHARACTERISTICS OF FERROELECTRIC SbSI(film) - Si - METAL DEVICES

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ABSTRACT

Antimony sulphoiodide (SbSI) films (0.1 to 0.5μm) have been prepared by flash evaporation on silicon substrates and field effect studies have been made in SbSI (film) - Si - Metal structure over a wide temperature range to cover both ferro- and paraelectric phases. Crystalline films could be obtained by keeping the substrate at 120°C. Post fabrication annealing at 100°C in Argon gas atmosphere considerably improved the quality of the films, as evinced by the increase in its dielectric constant. The current-voltage (I-V) characteristics show a rapid increase of current with applied voltage for low voltages and then show a tendency towards saturation at high voltages. The non-linear I-V characteristics at low voltages are due to the heterojunction formation at (n)Si - (p)SbSI films interface. The built in potential 0.23V estimated form I-V characteristics is supported by the photovoltage observed in this structure. At high voltages the current is controlled by the resistance of the films, and the room temperature resistivity of the film $\simeq 10^7$ ohm cm is in good agreement with reported values.

The C-V characteristics have been studied by an automatic C-V plotter and resemble that of MIS structure. The overall C-V curve is not affected markedly by the heterojunction, indicating the breakdown of heterojunction at high voltages. The capacitance in the accumulation region shows a broad peak ($\epsilon' = 64$) at about 20°C, confirming the ferroelectric nature of the film. The memory behaviour observed in C-V was noticed even upto 15°C above the transition temperature. However, the area of the loop was decreased in the paraelectric phase. This suggests that the interface effects giving rise to space charge build up play a dominant role in the hysteresis behaviour and the ferroelectric polarisation of the film plays a secondary role.

11:15 Session 8B1 Post Deadline
Chairman: L. E. Cross

8B1-1 Transduction Phenomena in Ferroelectric Polymers and Their Role in Transducer Performance, A.S. DeReggi and S. Edelman, National Bureau of Standards, USA

8B1-2 Ostegensis Induced By Bimorph Polyvinylidene Fluoride Films, J.J. Ficat, R. Durroux, M.J. Fauran, G. Escourrou, P. Ficat, C. LaCabanne Universite Paul Sabatier and F. Micheron L.C.R. Thomson C.S.F., France

8B1-3 S.A.X.S. Investigation of the Lamellar Structure in Rolled and Poled PVF_2 Thick Films, J.F. LeGrand and J. Lajzerowicz, Universite Scientifique et Medicale de Grenoble, France

8B1-4 Ferroelectric Materials In Dielectric Filtration, L. Benguigui and I.J. Lin, Technion-Israel Institute of Technology,Israel

8B1-5 Damage Resistant $LiNbO_3$ for High Power Modulators and Switches, G.E. Peterson, B.I. Greene, S.D. Poulsen, J. Jackel, and A.M. Glass, Bell Telephone Laboratories, U.S.A.

8B1-6 Domain Determination in PLZT Ceramics By Photo-Deposition of Silver, R.A. Lipeles, M.S. Leung, and M.B. Tueling, The Aerospace Corporation, USA

8B1-7 Practical Use of the Barhausen Effect in Ferroelectrics, V.M. Rudyak and N.M. Bolshakova, Kalin State University, U.S.S.R.

8B1-8 Soft Modes and Grain Size Effects in Ferroelectric Ceramics, M.R. Srinivasan, M.S. Multani, P. Ayyub and R. Vijayaraghavan, Tata Institute of Fundamental Research, India

Transduction Phenomena in Ferroelectric Polymers and Their Role in Transducer Performance

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The facts that (1) the piezoelectricity of polymers such as polyvinylidene fluoride (PVF_2) and related copolymers is largely secondary, and (2) that polymers in general have large thermal expansion coefficients, are responsible for transduction properties where piezo and pyroelectric effects may have to be considered together. In particular, in a PVF_2 transducer subjected to compression, the adiabatic compressional heating of the polymer is calculated to give a pyroelectric response amounting to approximately -18 percent of the isothermal piezoelectric response to the same compression. The thermal time constant governing the heat exchange between the polymer and its surrounding thus is an important design parameter. This time constant sets a crossover frequency between isothermal and adiabatic response. In the case where a polymer transducer is tightly coupled thermally to its surroundings and the surrounding material is chosen to have a much greater compressional heating coefficient than the polymer itself, thermal detection of pressure is possible. Several polymeric pressure transducers are discussed where the pyroelectric response can be made either incidental or a large part of the response.

OSTEOGENESIS INDUCED BY BIMORPH POLYVINYLIDENE FLUORIDE FILMS

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The first callus formation induced by piezoelectric polyvinylidene fluoride (PVDF) film has been reported in 1976 by SUSUKI. Nevertheless, the mechanism of action of induced osteogenesis remains still mysterious. So, the study of the influence of the nature of the stress exerted onto the piezoelectric film has been undertaken.

For this purpose, the osteogenic power of two kinds of piezoelectric PVDF films has been followed :

- "bulk" PVDF films sensitive to normal and shear stresses,
- "bimorph" PVDF films only sensitive to bending stresses.

PVDF films of various thicknesses - 175 μ, 250 μ , 450 μ - were implanted on a series of white new-zealand mature male rabbits. Each PVDF film was implanted round the right femoral diaphysis and a reference PVDF films round the controlateral femur. Osteogenesis was controlled by X rays and quantitative analysis of alkaline phosphatases in the blood. With bimorph films, a greatest amount of callus and an important remodilling of the cortical bone were observed. The new osteons are perpendicular to the cortical osteons, their orientation being probably governed by the lines of equal potential. The very promising behavior of these bimorph piezoelectric films, might announce a new generation of osteogen material.

S.A.X.S. INVESTIGATION OF THE LAMELLAR STRUCTURE IN ROLLED AND POLED PVF_2 THICK FILMS

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Several models have been proposed for calculating the piezoelectric and pyroelectric properties of polyvinylidene fluoride based on the lamellar structure of semicrystalline polymers (1), although there was little available information on the actual crystalline lamellae in PVF_2 piezofilms (2).

We report a small angle x-ray scattering investigation of piezoelectric PVF_2 thick films (β phase) biaxially oriented by rolling and simultaneous poling at the Laboratoire Central de Recherches THOMSON-C.S.F. (3). Several specimens, prepared under different conditions of poling and annealing, have been studied, and , for each specimen, the small angle scattering pattern has been recorded for different orientations of the piezofilm with respect to the x-ray beam.

The main results of this investigation are the following:
-The crystalline lamellae are piled up along the draw axis with a long period of 8.5 nm , but with a definite distribution of orientations which is not significantly affected by the poling process (the angle between the normal to a lamella and the draw axis ranges between 20 deg and 40 deg).
-The annealing of clamped films for one hour at 80 C results in some simplifications of the scattering pattern which are interpreted in terms of a better ordering of the lamellae with a noticeable increase of the long period (8.5nm to 9 nm).

These results provide new insights concerning :
-the mechanism of recrystallization ($\alpha \rightarrow \beta$) during the rolling process,
-the role of the depolarizing field (only a few lamellae are parallel to the polarization),
-the unlikelihood of rotation of a whole lamella during the poling process,
which lead to a new approach to preparation techniques for improving the piezoelectric properties of PVF_2.

(1) M.G. Broadhurst, G.T. Davis, J.E. McKinney and R.E. Collins, J. Appl. Phys. 49 (1978) 4992.
J.D. Clark and P.L. Taylor, Phys. Rev. Lett. 49 (1982) 1532.
(2) B.P. Kosmynin, Ye.L. Gal'perin and D.Ya. Tsvankin, Polymer Sci. USSR 14 (1972) 1530.
K. Nakagawa and Y. Ishida, J. Polym. Sci. Polym. Phys. Ed. 11 (1973) 2153.
J.M. Schultz, J.S. Lin, R.W. Hendricks, R.R. Lagasse and R.G. Kepler, J. Appl. Phys. 51 (1980) 5508.
A.J. Lovinger, Developments in crystalline polymers-1, (Appl. Sci. Publ., London, 1982), p.195.
(3) B. Servet, D. Broussoux, F. Micheron, (to be published).

FERROELECTRIC MATERIALS IN DIELECTRIC FILTRATION

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The dielectric filtration is based on removal of small particles from liquids, by application of inhomogeneous electric fields. The particles which are drifted towards regions with higher gradient by the dielectrophoretic force, are trapped onto a matrix. This matrix has a double function: a) trapping the particles b) creation or enhancement of the field gradient, depending if the electric field is uniform or not, without the matrix. We describe in detail the filtration process in the case of a matrix made of insulating balls. We found that this filtration method is very efficient, in particular by removing all types of particles (metal, plastic, ceramics, minerals) from insulating liquids. We show that the best way of producing high gradient field with relatively low field is to use ceramic balls of ferroclectric materials. Due to the high permittivity of the balls, the lines of force tend to concentrate in the balls and generate a non-uniform field in their vicinity.

Damage Resistant $LiNbO_3$ for High Power Modulators and Switches

by

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ABSTRACT

Titanium diffusion into $LiNbO_3$ is the most commonly used technique for the fabrication of optical waveguides for hybrid integrated optical devices. Both ordinary and extraordinary waves can be guided and fabrication of complex guided wave structures is relatively straightforward. However, Ti diffused guides suffer from a high photorefractive sensitivity ("optical damage") which makes them of limited use for application in the visible spectrum.

For certain device applications we wished to switch, gate and modulate a high power, mode locked, ring dye laser which operates at 620 nm. This laser has a repetition rate of 110 MHz, a pulse width of 0.2 psec and an average power of 20 mW. When focused into a planar waveguide using a 30 cm lens and a prism coupler the average optical intensity inside the guide is about $5kw/cm^2$ and the peak pulse intensity is about $5x10^8$ w/cm^2. A titanium diffused $LiNbO_3$ optical wave guide will not operate under these conditions for more than a few seconds. It was recently shown that the introduction of hydrogen into a $LiNbO_3$ waveguide during Ti diffusion at 900 to 1100 degrees reduces the photorefractive sensitivity by about two orders of magnitude. It has also been found that large concentrations of hydrogen can be exchanged for Li ions by immersion of $LiNbO_3$ in low temperature proton sources such as acids or hydrate melts. Proton exchange results in waveguides having very large increases of the extraordinary index. Because of the low temperature required for this latter process, fabrication of integrated devices are readily made simply by masking the surface during exchange.

A number of modulators, switches and gates have been constructed using proton exchange and rather elementary masking methods. We find that they operate satisfactorily with the ring laser previously mentioned.

DOMAIN DETERMINATION IN PLZT CERAMICS BY PHOTO-DEPOSITION OF SILVER

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Knowledge of domain structure and orientation is essential to understanding the electro-optical properties of ferroelectric lead lanthanum zirconate titanate (PLZT) ceramics. Conventional thermal and acid etching techniques can provide information on grain and domain structures. In this paper, a technique using photodeposition of silver for studying the ferroelectric domain orientation in PLZT ceramics is presented. The technique makes use of the differences in affinity of the silver ions to adsorb onto different domain orientations to decorate the domains in PLZT. The results of using this technique to decorate electrically and thermally depoled PLZT as well as PLZT poled in the opposite directions are discussed in detail. The use of this technique to study the effects of processing conditions and grain size on the ferroelectric domain structure in a variety of PLZT materials will be reported. This technique can also be used to study domain coalescence as a function of the applied field. This type of information is needed to analyze the read and write resolution and contrast of optical recording devices based on PLZT ceramics.

PRACTICAL USE OF THE BARKHAUSEN EFFECT IN FERROELECTRICS

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The connection of Barkhausen effect (BE) to the domain structure (DS) and hysteresis loop parameters, its high sensitivity to various external influences, reproducibility for a given sample's state provide the basis for its application in investigations of ferroelectrics on a level with putting into effect measurements of a number of practically important physical quantities.

Considerable body of information about the temporal characteristics of the polarization reversal process and its peculiarities at different polarization curve and hysteresis loop stages is provided by the distribution of BE jumps on field and time. The high sensitivity of BE to external influences provides its use as a sensitive indicator of the latter.

With the aid of thermal BE (TBE) it is possible to study the kinetics of DS realignment in ferroelectric crystals and ceramics at continous temperature changing in the absence or constancy of external electric fields. The polarity of TBE jumps enables one to separate the competing contributions of polarization and depolarization processes even in the case when they proceed simultaneously.

BE effect data are of advantage not only from the physical but also practical standpoint in view of growing applications of ferroelectric materials in various devices working in broad temperature ranges.

A number of practical BE devices is proposed utilizing: a) coercive field measurements, b) studying the intensity of ceramics DS realignment in a broad temperature range, c) measurement of temperature, d) ferroelectric BE tachometer.

SOFT MODES AND GRAIN SIZE EFFECTS IN FERROELECTRIC CERAMICS

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Abstract: It is pointed out that the grain size effects on the transition parameters in ferroelectric ceramics can be explained on the basis of size effects on the ferroelectric properties of the constituent grains.

The increased use of ferroelectric ceramics in practical applications has led to many experimental investigations concerning the effects of grain size on the dielectric behaviour. For grain sizes in the range of 1-5 μm, it is now established that with decreasing grain size (a) ϵ_{max} decreases, (b) the dielectric peak broadens and (c) the ferroelectric transition shifts to higher temperatures.[1,2] The observed experimental data has been mainly accounted for the basis of the motion of domain walls within each grain, the space charge effects and the diffuse phase transition model. While certainly not neglecting these factors we propose that the size effects on the ferroelectric properties of individual grains also have to be taken into account. Känzig's observations show that the tetragonal distortion in fine-grained $BaTiO_3$ powders reduces for particle sizes below 5 μm.[3] Also the tetragonal distortion persists at temperatures higher than the Curie temperature of the bulk crystal. Känzig also postulates that ferroelectric semiconductors like $BaTiO_3$ and PZT can exhibit a surface layer of thickness 0.1 - 0.01 μm.[4] Further, the surface layer has lower dielectric constant compared with that of the bulk.[5] The surface-to-volume ratio increases with the decrease in grain size, resulting in the lowering of dielectric constant. The actual contribution from the surface layers will however depend upon the porosity in the ceramic, sintering conditions, etc.. From the lattice-dynamical view point, the decrease in dielectric constant at lower grain sizes can occur due to the breakdown of cyclic Born-von-Karman condition. In grains of small size the cyclic Born-von-Karman condition has to be replaced by

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REFERENCES

1. K. Okazaki and K. Nayata, J. American Ceramic Society, 56, 82(1973).
2. H.T. Martirena and J.C. Burfoot, J. Phys, C 7, 3182 (1974).
3. M. Anliker, H.R. Brugger and W. Kanzig, Helv. Phys. Acta, 27, 99 (1954).
4. W. Kanzig, Phys. Rev., 98, 549 (1955).
5. A.K. Coswami, J. Appl. Phys., 40, 619 (1969).
6. G. Shirane, J.D. Axe, J. Harada and A. Linz, Phys. Rev., 2B, 3651 (1970).
7. V.P. Dudkevich, VI.M. Muhkhortov, Yu.I. Golovko, V.A. Bukreev, Vas.M. Mukhortov, Yu.G. Sindeev and E.C. Ferenko, Sov. Phys. Solid State, 23, 347 (1981).
8. D.A.G. Bruggeman, Ann. Phys., 24, 636 (1935).
9. G.A. Samara, Phys. Rev., 151, 378 (1966).
10. G.W. Timco and H.H. Schloessin, Ferroelectrics, 11, 409 (1976).
11. H. Diamond, J. Appl. Phys., 32, 909 (1961).

the boundary condition on the surface. This has the effect that the phonon wave vector becomes discrete and the lattice spectrum no longer includes vibrations with the wave vectors in the range $|K| < \pi/D$ where D is the size of the grain.

In ferroelectrics, the dominant contribution to ϵ_{max} arises from the K = 0 soft polar mode. It is therefore sufficient to consider size effects only on those optic modes which have strong dispersion at K = 0. In $BaTiO_3$ only the optic mode having K// [110] shows strong dispersion at K = 0. The dispersion of the soft mode is of the form

$$\hbar^2\omega_{TO}^2(K) = \hbar^2\omega_{TO}^2(0) + \alpha K^2 \qquad (1)$$

where $\hbar\omega_{TO}(0) = (4.5 \pm 1.0)\ 10^{-3}$ ev and $\alpha = 5.1 \times 10^{-4} eV^2 A^2$ at T = 300°K.[6]

Applying the Lyddane-Sachs-Teller relationship, which is valid in the presence of spatial dispersion and unaffected by boundary conditions, one finds[7]

$$\epsilon_0(D) = \epsilon_0(\infty)/(1 + \beta D^2) \qquad (2)$$

where $\epsilon_0(\infty) = S\epsilon_\infty\omega_{LO}^2(0)/\omega_{TO}^2(0)$ is the value of ϵ_0 in the limit $D \to \infty$; ϵ_∞ is the high-frequency dielectric constant for the bulk crystal, the constant S allows for the contribution from the remaining lattice vibrations and $\beta = \alpha\pi^2/\hbar^2\omega_{TO}^2(0)$. Equation (2) clearly shows that the dielectric constant maximum has to decrease with the decreasing grain size. In Fig. 1 the curve A denotes the theoretical value obtained for a $BaTiO_3$ ceramic employing Bruggeman's formula.[8] Curves B, C and D denote theoretical values for $BaTiO_3$ grains of sizes 150Å, 100Å and 50Å respectively. Equations (1) and (2) enable us to estimate the grain size for which size effects become important. Allowing for the errors in the determination of parameters in equation (1) it appears that these effects are noticeable only when grain sizes are $< 0.1\mu m$. It is also possible that due to crystallographic inhomogenities within a grain, these effects show up even for grain size larger than this.

SOFT MODE AND GRAIN SIZE

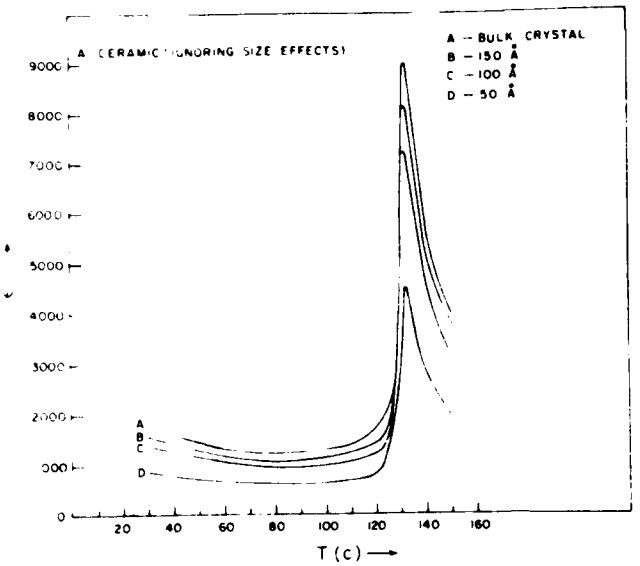


FIGURE 1. Size effects on dielectric behaviour.

The pressure effects on the dielectric behaviour of $BaTiO_3$ and PZT ceramics indicate a decrease in the dielectric constant, downward shift of the transition temperature and broadening of the dielectric peak with the increase of pressure.[9, 10] With the decrease in the size of the grain there is a lattice expansion and the transition temperature shifts upwards.[3] Thus the grain size effects could be considered as negative pressure effect.

The broadening of the dielectric peak with the decreasing grain size can be accounted for by assuming a gaussian distribution of Curie temperature for the grains as in Diamond's model.[11] In Diamond's model such a distribution of Curie temperature can occur as a result of chemical inhomogeneities and strains. We propose that in addition to these factors the grain size distribution within the ceramics also contributes the distribution of Curie temperatures. Since the size effects become predominant at lower grain sizes, it is reasonable to assume that the width of the distribution of Curie temperatures increases with the decrease in the mean grain size. This accounts for the broadening of the dielectric maximum at lower grain sizes.

11:15 Session 8B2 Post Deadline
Chairman: R.E. Newnham

8B2-1 Multilayer Ceramic Capacitor Design - Magic, Mystery or Fact, D. Graudons, Centre Hall, Pennsylvania, USA

8B2-2 A New Technique for Ultra Low Frequency Measurement of Dielectric Properties, Zhang Liang-Ying, Yao Xi, and L.E. Cross, The Pennsylvania State University, USA

8B2-3 Elastic and Dielectric Nonlinearities of Piezoelectric Ceramics, H. Beige Martin-Luther Universitat, German Democratic Republic

8B2-4 Equivalent Circuit of Piezoelectric Ceramic Transducer With Losses, J.D. Chang and Q.D. Luan, Peking University, Peoples Republic of China

8B2-5 Hydrothermal Crystallization of Ferroelectrics and their Properties, V.I. Popolitov, V.F. Peskin, and R. Ch. Bichurin Academy of Sciences, U.S.S.R.

8B2-6 Synthesis of Single Crystals $SbTiNbO_3$, V.I. Popolitov and V.F. Peskin, Academy of Sciences, USSR

8B2-7 Influence of Cubic Anisotropy in Dipole-Dipole Interactions on Structural Phase Transitions Using the Renormalization Group Transformation, G. Verstraeten, Instituut voor Theoretische Natuurkunde, Netherlands

8B2-8 Positron Annihilation in Ferroelectric Ceramics $PbTiO_3$ Doped with La and Mn, Li Long-tu, He Yuanjin, and Yu Welzhong, Tsinghua University, Peoples Republic of China

8B2-9 Memory Effects in the Structure of Silicon Single Crystal-Ferroelectric Film, S.V. Tolstousov, V.M. Mukhortov, V.I. Mukhortov, V.P. Dudkevich, and Eu. G. Fesenko, Rostov State University, USSR

8B2-10 Techniques of Obtaining Ferroelectric Films and Their Physical Properties, V.P. Dudkevich and Eu. G. Fesenko, Rostov State University, USSR

MULTILAYER CERAMIC CAPACITOR DESIGN - MAGIC, MYSTERY OR FACT

D. Graudons, Centre Hall Pennsylvania, USA

ABSTRACT

A ten year study of multilayer ceramic capacitor technology from a Ceramic Engineering point of view is presented for consumers interested in the origin of their components.

The thought involved, standard equations and processing parameters are overviewed for understanding of the problems to be overcome in order to consistantly deliver a quality product.

It is realized that there are many ways of doing the same thing and concludes with a medical analagy of care and prevention being the best doctor.

A NEW TECHNIQUE FOR ULTRA LOW FREQUENCY MEASUREMENT OF DIELECTRIC PROPERTIES

Zhang Liang-Ying, Yao Xi and L.E. Cross

Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16802

In this modification of the constant voltage ramp method, the rate of change of voltage applied to the dielectric under study is maintained constant under computer control. At any instant of time, the current measured in a high sensitivity electrometer I_T is the sum of a conduction current I_c and a dielectric displacement current I_D. The conduction component I_c is given by

$$I_c = V/R_i$$

where R_i is an effective instantaneous resistance at the voltage level V. The displacement current I_D is

$$I_D = \frac{dQ}{dt}$$

where the stored charge Q can be related to the dimensions and dielectric properties of the sample under study.

Clearly at any time when V = 0, the conduction component of current must go to zero. Thus by starting the voltage ramp from a fixed positive or negative voltage, ramping at a fixed rate to zero voltage and measuring the instantaneous current exactly at zero crossing the conduction may be eliminated and the pure displacement current explored.

The method has been used to examine the time dependence of the dielectric properties in polystyrene, mica, lithium niobate, soft PZT and in specific PLZT compositions. By varying the initial applied voltage, the initial voltage soaking time and the voltage ramp rate a rather complete examination of the dielectric properties at low frequencies can be accomplished.

Elastic and dielectric nonlinearities of piezoelectric ceramics

H. Beige

Sektion Physik, Martin-Luther-Universität Halle-Wittenberg,
Halle (Saale), German Democratic Republic

Piezoelectric ceramics are mostly specified for small signal applications by the linear coefficients. However, an unambiguous characterization of ceramics, which are to be operated at high mechanical or electric power level cannot be given by these means. There is still an urgent need to improve the characterization of piezoelectric ceramics.

The aim of the present paper is to give a contribution for solving this problem by means of the determination of higher order elastic and dielectric coefficients.

The nonlinear elastic coefficients were calculated from the shift of the resonance frequency of longitudinal vibrations of bars in dependence on the amplitude of the driving force. The same principle is used for the determination of the nonlinear dielectric coefficients. The sample is integrated in a series resonant circuit and the change of the resonance frequency in dependence on the amplitude of the driving force is measured.

It was observed that after increasing the driving force beyond a critical value the small signal resonance was lowered. From the critical amplitude beyond which irreversible processes occure in the ceramic a critical mechanical stress and a critical electric field strength can be calculated.

For different types of piezoelectric ceramics the temperature dependence of the linear coefficients, of the nonlinear elastic coefficients, of the nonlinear dielectric coefficients, of the critical mechanical stress and of the critical electric field strength will be presented.

The results show that the determination of the nonlinear elastic and dielectric coefficients and of the critical mechanical stress and electric field strength gives a helpful contribution to the characterization of ceramics, which are to be operated at high mechanical and electric power level.

Equivalent Circuit of Piezoelectric Ceramic Transducer With Losses

Abstract

J. D. Chang & Q. D. Luan
Radio-Electronics Department of Peking University

When people deducing the equivalent circuit of a piezoelectric ceramic transducer, generally the losses were neglected at the outset. After they established the equivalent circuit, they added a lumped mechanical resistance and electric resistance in the equivalent circuit to represent the losses. These mechanical and electrical resistances could only be determined by experimental methods, and could not be deduced exactly theoretically. On the other hand less consideration was given to the losses in the electromechanical energy conversion.

Recntly investigators have begun to use complex dielectric constants, complex elastic coefficients and complex piezoelectric coefficients to represent dielectric losses, elastic losses and losses of electromechanical conversion respectively. If this method of approach were used then the equations would become comlex, i. e.

$$\begin{bmatrix} S \\ D \end{bmatrix} = \begin{bmatrix} s^E & d^t \\ d & \varepsilon^T \end{bmatrix} \begin{bmatrix} T \\ E \end{bmatrix}$$

$$\begin{bmatrix} T \\ E \end{bmatrix} = \begin{bmatrix} c^D & -h^t \\ -h & \beta^S \end{bmatrix} \begin{bmatrix} S \\ D \end{bmatrix}$$

$$\begin{bmatrix} T \\ D \end{bmatrix} = \begin{bmatrix} c^E & -e^t \\ e & \varepsilon^S \end{bmatrix} \begin{bmatrix} S \\ E \end{bmatrix}$$

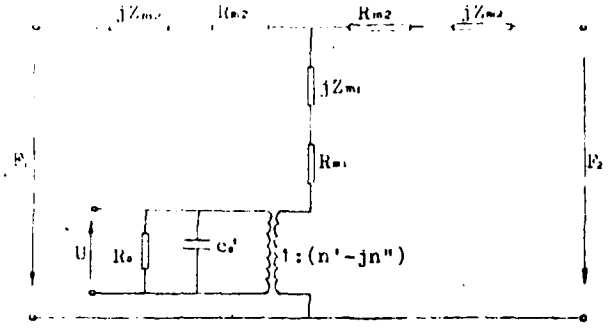
$$\begin{bmatrix} S \\ E \end{bmatrix} = \begin{bmatrix} s^D & g^t \\ -g & \beta^T \end{bmatrix} \begin{bmatrix} T \\ D \end{bmatrix}$$

Here

$$S = s' - js'', \quad c = c' + jc''$$
$$\varepsilon = \varepsilon' - j\varepsilon'', \quad \beta = \beta' - j\beta''$$

$$d = d' - jd'', \quad h = h' + jh''$$
$$s = s' - js'', \quad e = e' + je''$$

In this paper we deduced the equivalent circuit of a length-extensional bar of piezoelectric ceramic with losses starting from the complex piezoelectric equations.



Here

$$R_{m1} = \frac{\rho m d}{D}\left(\frac{2}{\rho s_{11}'}\right)^{\frac{1}{2}}\left\{\frac{(D+1)^{\frac{1}{2}}\,\mathrm{shk''l}\,\cos k'l + (D-1)^{\frac{1}{2}}\,\mathrm{chk''l}\,\sin k'l}{\mathrm{ch2k''l} - \cos 2k'l}\right\}$$

$$Z_{m1} = \frac{\rho m d}{D}\left(\frac{2}{\rho s_{11}'}\right)^{\frac{1}{2}}\left\{\frac{(D-1)^{\frac{1}{2}}\,\mathrm{shk''l}\,\cos k'l - (D+1)^{\frac{1}{2}}\,\mathrm{chk''l}\,\sin k'l}{\mathrm{ch2k''l} - \cos 2k'l}\right\}$$

$$R_{m2} = \frac{\rho m d}{D}\left(\frac{1}{2\rho s_{11}'}\right)^{\frac{1}{2}}\left\{\frac{(D+1)^{\frac{1}{2}}\,\mathrm{shk''l} - (D-1)^{\frac{1}{2}}\,\sin k'l}{\mathrm{chk''l} + \cos k'l}\right\}$$

$$Z_{m2} = \frac{\rho m d}{D}\left(\frac{1}{2\rho s_{11}'}\right)^{\frac{1}{2}}\left\{\frac{(D-1)^{\frac{1}{2}}\,\mathrm{shk''l} + (D+1)^{\frac{1}{2}}\,\sin k'l}{\mathrm{chk''l} + \cos k'l}\right\}$$

$$C_0' = \frac{ml}{d}\left\{\varepsilon_{33}' - \frac{s_{11}'\,(d_{31}'^2 - d_{31}''^2) + 2s_{11}''d_{31}'d_{31}''}{s_{11}'^2 + s_{11}''^2}\right\}$$

$$\frac{1}{R_0} = \omega\frac{ml}{d}\left\{\varepsilon_{33}'' - \frac{2s_{11}'d_{31}'d_{31}'' - s_{11}''\,(d_{31}'^2 - d_{31}''^2)}{s_{11}'^2 + s_{11}''^2}\right\}$$

In these formulas

l — length of the bar

w — width of the bar

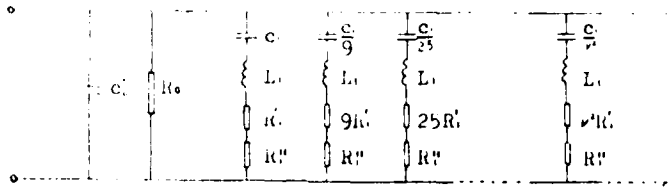
t — thickness of the bar

and

$$\nu = \left[1 + \left(\frac{s_{12}^{E}}{s_{11}^{E}}\right)^{2}\right]^{\frac{1}{2}}$$

By means of this, as an example, this paper shows how we implement general equivalent circuit of tranducers with losses.

As an application of these deduced results, the equivalent circuit of a free resonator is obtained by analysing its free vibration condition.



Here

$$C_0' = \frac{ml}{d}\left[\varepsilon_{33}' - \frac{s_{11}'(d_{31}'^{2} - d_{31}''^{2}) + 2s_{12}''d_{31}'d_{31}''}{s_{11}'^{2} + s_{12}''^{2}}\right]$$

$$\frac{1}{R_0} = \omega\frac{ml}{d}\left[\varepsilon_{33}'' - \frac{2s_{12}'d_{31}'d_{31}'' - s_{12}''(d_{31}'^{2} - d_{31}''^{2})}{s_{11}'^{2} + s_{12}''^{2}}\right]$$

$$C_1 = \frac{8ml}{\pi^2 d}\left[\frac{(d_{31}'^{2} - d_{31}''^{2})^2 + 4d_{31}'^{2}d_{31}''^{2}}{s_{11}'(d_{31}'^{2} - d_{31}''^{2}) + 2s_{12}''d_{31}'d_{31}''}\right]$$

$$L_1 = \frac{\rho l d}{8m}\left[\frac{(s_{11}'^{2} - s_{12}''^{2})(d_{31}'^{2} - d_{31}''^{2}) + 4s_{11}'s_{12}''d_{31}'d_{31}''}{(d_{31}'^{2} - d_{31}''^{2})^2 + 4d_{31}'^{2}d_{31}''^{2}}\right]$$

$$R_1' = \frac{\pi^2 d}{8\omega ml}\left[\frac{2s_{11}'d_{31}'d_{31}'' - s_{12}''(d_{31}'^{2} - d_{31}''^{2})}{(d_{31}'^{2} - d_{31}''^{2})^2 + 4d_{31}'^{2}d_{31}''^{2}}\right]$$

$$R_1'' = \frac{\omega\rho l d}{8m}\left[\frac{2s_{11}'s_{12}''(d_{31}'^{2} - d_{31}''^{2}) - 2d_{31}'d_{31}''(s_{11}'^{2} - s_{12}''^{2})}{(d_{31}'^{2} - d_{31}''^{2})^2 + 4d_{31}'^{2}d_{31}''^{2}}\right]$$

the real part and imaginary part of these complex coefficients can be calculated conveniently by these formulas, if the admittance circle diagram is measured. This paper gives the measured data of these complex coefficients and their approximate relationship.

The results given in this paper can also be used to calculate other vibrators where the electric field is parallel or perpendicular to the vibration direction and from which we obtain a method to measure the real part and imaginary part of other complex coefficients.

HYDROTHERMAL CRYSTALLIZATION OF FERROELECTRICS AND THEIR PROPERTIES

V.I.Popolitov, V.F.Peskin, A.Ch.Bichurin
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Leninsky pr. 59, Moscow, 117333,
USSR

The present work regards hydrothermal conditions of synthesis and growth of the crystals with different structure types, such as stibium tantalite type compounds [1] and antimonites with the common formula $Me_3Sb_5O_{12}$ (Me- In, Se, La, Pr, Tb, Yb)

There have been studied the regularities of hydrothermal growing on a seed of mixed single crystals on stibium ortoniobate basis in the system Sb_2O_3-Sb_2O_5-Nb_2O_5-R-H_2O (R-the solvent) in relation to various physical-chemical parameters. It has been shown that in the system under study the formation of the mixed single crystals with the composition $Sb(Sb_xNb_{1-x})O_4$ (where x- 0,08; 0,14; 0,26), wich could be regarded as the solid solutions of the replacement, took place. Mixed single crystals have better structural and optical perfection, than $SbNbO_4$ [2] single crystals. They are more transparent in the visible range and are characterized by the better formed edge of self-absorbtion. The dielectrical characteristics have been studied and it has been shown, that for $Sb(Sb_xNb_{1-x})O_4$ with x=0,26 the dielectrical constant at 20 °C was: for ε_a=40, ε_b=35, ε_c=140; for $SbNbO_4$ crystal (x=0) ε_c=200 at 20 °C. The increase of Sb^{5+} containment from x=0 to x=0,26 leads to the noticeable electroconductivity lowering. The table presents the temperatures of phase transitions and dielectrical characteristics of the crystals.

x	0	0,08	0,14	0,26
T_c	415	310	230	180
T_{max}	400	305	230	180
tg (20 °C)	0,02	0,01	0,01	0,003

It is seen from the table, that the variation of crystallization parameters makes possible to change physical properties of the crystals, what has a certain practical interest, for instance, in the selection of the optimum combination of the above characteristics for stibium niobate application as pyrodetectors. The regularities of $Me_3Sb_5O_{12}$ single crystals

synthesis in various hydrothermal media have been investigated. There have been found out the optimum conditions of their formation from the yeild and perfection points of view.

The dielectrical, piezoelectrical, pyroelectrical, electrooptical and some other physical properties of the obtained $Me_3Sb_5O_{12}$ crystals have been studied. $In_3Sb_5O_{12}$ and $Se_3Sb_5O_{12}$ compounds have displayed the effect of the electroacoustic echo with the large relaxation time - 160 and 140 msec correspondingly. $Me_3Sb_5O_{12}$ compounds with rare earth cation (except Yb) display polar distortion at room temperature and irreversible phase transitions in the range of 380-420°K.

References

1. V.I.Popolitov, A.N.Lobachev, V.F.Peskin. Antiferroelectrics, ferroelectrics and pyroelectrics of a stibiotantalite structure. Ferroelectrics, 40, p.9-16, 1982.
2. V.I.Popolitov, V.F.Peskin, A.N.Lobachev i dr. Vyrashivanie chistych i legirovannych primesiami monocrystallov $SbNbO_4$ i ich pyro- i segnetoelectricheskie svoystva. Crystallographia, t.24, v.4, s.798-803, 1979.

SYNTHESIS OF SINGLE CRYSTALS $SbTiNbO_6$

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USSR

The discovery of the ferroelectric properties of group ABO_4 (A-Sb, Bi; B-Nb, Ta, Sb^{5+}) [1] stimulated the further works on obtaining and research of single crystals of the $SbTiNbO_6$. The single crystals of the $SbTiNbO_6$, studied in the present work, were grown by the hydrothermal method.

It was find out, that the maximum yield of single crystals depend on the concentration and the composition of the solvents, the ratio of the starting components in the nutrient, partial pressure of oxigen, the value of Eh-pH of the medium, temperature and its gradient. Concentrations of Sb, Nb, Ti (in weight%) in single crystals $SbTiNbO_6$ were found by a x-ray local spectral analysis method with the aid of the spectrometer "Cameka". The obtained values are in good agreement with the values calculated from the formulas of their composition.

The dielectric characteristics of single crystals were measured on platelets in the direction of polar axic [001]. Under investigation it was established that monocrystals $SbTiNbO_6$ are in spontaneously polarized state and demonstrate sharp maximum of E at 270-280°C. The single crystals possess a pyroelectric effect in the region from -180 to +280°C.

References

1

1. V.I.Popolitov, A.N.Lobachev, V.F.Peskin. Antiferroelectrics, ferroelectrics and pyroelectrics of a stibiotantalite structure. Ferroelectrics, 40, p.9-16, 1982.

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INFLUENCE OF CUBIC ANISOTROPY IN DIPOLE-DIPOLE INTERACTIONS ON STRUCTURAL PHASE TRANSITIONS USING THE RENORMALIZATION GROUP TRANSFORMATION

The critical behaviour of ferroelectrics is studied for $T \geq T_c$ and for zero electric field, by therenormalization group techniques in d=3 dimensions. The model hamiltonian we used contains an isotropic exchange coupling and a dipolar interaction with strong cubic anisotropy. The propagators are expanded in spherical harmonical functions up to second order of the quartic coupling constants.

A quadratic anisotropic fixed point is found to be stable for the cubic anisotropic scale field. Experiments on $BaTiO_3$ and $KTaO_3$ are compared with our results.

Positron Annihilation In Ferroelectric Ceramics $PbTiO_3$ Doped with La and Mn

Li Long-tu
(Department of Chemistry and Chemical Engineering)

He Yuanjin, Yu Weizhong
(Department of Physics)

(tsinghua University)
Peoples Republic of China

Abstract

This paper refers to positron annihilation in ferroelectric ceramics. The positron lifetime spectra of the ferroelectric ceramics $PbTiO_3$ doped with La and Mn have been measured . A fast-timing system was used for positron lifetime measurments in $PbTiO_3$. The resolution ability of the spectrometer (FWHM) was 280Ps. The room temperature was maintained at $23^{\circ}C \pm 1^{\circ}C$. The positron source ^{22}Na had 70 μCi activity. The total counts of annihilation gamma quanta recorded in one spectrum were $(5\text{-}8) \times 10^5$.

The Composition of the Sample was $(Pb_{1-1.5x} La_x \square_{0.5x})(Ti_{0.98} Mn_{0.02})O_3$. where, X were 0.01-0.10, $\square$ presents Pb^{+2} vacancies. The size of specimens was $20 \times 20 \times 1\ mm^3$. The experimental results had been shown that the mean lifetime τ_m and positron trapping rates K increased with the doped La amounts before $x \leq 0.04$, and then seemed to be retained. It gave an evidence of the trapping effect of the Pb vacancies created by doping with La^{+3}, and La^{+3} does occupy the A site of ABO_3 perovskite structure. The lifetime of positrons in Pb^{+2} vacancies was estimated to be 304Ps, and ν , the the volume rate of trapping by Pb^{+2} vacancies, was about $3.75 \times 10^{-11} cm^3/s$ It is clear from the experiments that the positron annihilation technique is a efficient method for studing of defect structure of ferroelectric ceramics.

MEMORY EFFECTS IN THE STRUCTURE OF SILICON SINGLE CRYSTAL - FERROELECTRIC FILM

S.V. Tolstousov, Vas.M.Mukhortov, Vl.Mukhortov, V.P.Dudkevich, Eu.G.Fesenko.

Department of Physics, Rostov State University, Rostov-on-Don, USSR.

Polycrystalline films of $Ba_xSr_{1-x}TiO_3$ where x=0.6-1.0 with the thickness 1-7 μm deposited on (111) and (100) cuts of Si by cathode sputtering[1] were studied.
Their composition, structure, volt-farad characteristics, dielectric hysteresis loops and piezoactivity were studied.

On the volt-farad characteristics there were observed hysteresis phenomena with two stable (for more than 2 months) states C_{max} and C_{min} at U=0, as on $Bi_4Ti_3O_{12}$ films [2]. In this case the relation Cmax/C min was far larger than in [2] and reached 8-12, that is close to the theoretic estimate. A unidirectivity of transition to these states, and also the generation effect in the ultrashort wave range was revealed.

On the specimens studied dielectric hysteresis loops with strong unipolarity were observed, similar to those in [3] which transformed into symmetric ones with illumination.
The spontaneous polarization determined by the loops was 6 μC/^{2}.

All the specimens studied revealed piezoactivity without any preliminary polarization, the piezoactivity in the state Cmin being maximum, and in the state C max-minimum. The piezocoefficient d_{33}, measured by the static and quasistatic methods was $8 \cdot 10^{-12}$ C/N.

All the aggregate of peculiarities is accounted for in terms of a supposition about the possibility of injecting the carriers

from Si into the (Ba, Sr) TiO_3 film depending on the direction of spontaneous polarization field and external electric field.

References

1. V.M. Mukhortov, V.P.Dudkevich, V.S.Bondarenko, V.S.Mikhalevsky, Yu.G.Fesenko. Izv. Akad.Nauk SSSR, inorganic materials 11, 2010, 1975.
2. S.Y.Wu-I EEE Trans. Electron Devices, E.D.-21, 499, 1974.
3. I.K.Park, M.W. Grannemann. Ferroelectrics, 10, 217, 1976.

TECHNIQUES OF OBTAINING FERROELECTRIC FILMS AND THEIR PHYSICAL PROPERTIES.

V.P.Dudkevich and Eu.G.Fesenko Department of Physics,
Rostov State University, Rostov-on-Don, USSR

An analysis has been carried on and a systematics is given of the methods of obtaining ferroelectric films. It is shown that only the techniques of vacuum crystallization combined with the solid microelectronics provide the formation of highly thin films needed for research purposes and practical application. On the basis of original and literature data about the physical-chemical processes related with the formation of films, the data about their composition, structure, microstructure and physical properties , it has been established that all the familiar modifications of vacuum evaporation are unfit for reproducible obtaining of ferroelectric films of complex oxides without any further high-temperature treatment: various modifications of cathode sputtering are perspective.

The peculiarities of revealing ferroelectric properties in films with different degree of structure ordering (X-ray-amorphous, polycrystalline, textural, heteroepitaxial) are illustrated and discussed. In particular, it is shown that the blurring of ferroelectric phase transition, alongside with other known factors is determined by the sizes of coherent scattering regions and the value of 2 nd order microdeformations (the integral measure of extended structure defects).

For the first time, a complete set of data on the heteroepitaxial films is given, which includes the data on spontaneous deformation and its temperature dependence, on the peculiarities of domain structure, on piezomoduli, dielectric nonlinearity, etc.

A conclusion has been made about the possibility of applying ferroelectric films as active elements in microelectronics.

2:00 p.m. SESSION 9A: Materials (Fracture)
Chairman: S.T. Liu

9A-1 Fracture of Ferroelectric Ceramics: A Review- S. W. Freiman, R.F. Cook and B.R. Lawn, National Bureau of Standards and R.C. Pohanka, Office of Naval Research, USA

9A-2 Internal Stress Anisotropies Induced by Electric Field in Lanthanum Modified $PbTiO_3$ Ceramics - T. Yamamoto, H. Igarashi and K. Okazaki, National Defense Academy, Japan

9A-3 Fracture Mechanics Parameter and Strength Evaluation of Piezoelectric Ceramic Plate - H. Niitsuma and N. Chubachi, Tokyo University, Japan

9A-4 The Dynamic Strength of Piezoelectric Ceramics - R.C. Pohanka and P.L. Smith, Office of Naval Research and J. Pasternak, Naval Research Laboratory, USA

9A-5 Analysis of Soldering-Induced Cracking of $BaTiO_3$ Ceramic Capacitors - J.A. Van Den Avyle and J.J. Mecholsky, Sandia National Laboratories, USA

Fracture of Ferroelectric Ceramics: A Review

S. W. Freiman, R. F. Cook and B. R. Lawn
National Bureau of Standards
Washington, DC

R. C. Pohanka
Office of Naval Research
Arlington, VA

In this paper we will discuss the current state of understanding of the fracture toughness and strength of $BaTiO_3$ and $Pb(Zr_x,Ti_{(1-x)})O_3$ as a function of crystal structure and grain size. It will be shown that crack growth resistance can be affected by a combination of twinning, microcracking and phase transformations. Microstructural stresses generated by the paraelectric to ferroelectric phase transformation are shown to be important in determining the strengths of these materials when flaw sizes are $\lesssim$ 10 G, where G is the average grain size. Emphasis will be placed on newly developed experimental and analytic techniques which can be used to make a quantitative determination of these internal stresses as a function of the flaw-size to grain-size ratio. Specifically, by placing hardness indentations in the material and then fracturing the specimens in flexural tests, the size and severity of the failure producing flaws can be controlled. The change in fracture strength as the flaw size is varied gives a measure of the various stress fields acting on the flaw.

Internal Stress Anisotropies Induced by Electric Field in Lanthanum Modified $PbTiO_3$ Ceramics

T. Yamamoto, H. Igarashi and K. Okazaki
Dept. of Electrical Engineering, The National Defense Academy, Yokosuka, 239 Japan

Abstract

Lantnanum modified lead titanate, $Pb_{1-1.5\cdot X}La_XTiO_3$, ceramics with tetragonal and cubic structure were hot-pressed and mechanical properties were measured using a micro-indentation technique by changing the load of indent. The internal stresses were evaluated as a function of the crystal tetragonality, c/a. The internal stress increased linearly with increasing c/a in the tetragonal region and diminished to zero at near cubic region c/a =1.000 ; the values for the c/a=1.028 and 1.000 samples were 150 and 0 MN/m^2, respectively. In the tetragonal region, an anisotropy in the internal stress induced by residual strains generated by applying a DC field of 3 KV/mm were found and the internal stresses in the directions perpendicular and parallel to the poling field were 151 and 35 MN/m^2 in the c/a=1.024 specimen, respectively. Moreover, the anisotropies in the internal stress were changed by the strength of DC poling field of 0 to 2.5 KV/mm in the c/a=1.028 specimen. The results were explained by the crack-extentional and-compressive force, respectively. Furthermore, an aging change of the anisotropic internal stress was found and discussed with relationship between the internal bias field and internal stress and with the microstructure obsrevation using a scanning electron microscope.

Fracture Mechanics Parameter and Strength Evaluation of Piezoelectric Ceramic Plate

Hiroaki NIITSUMA and Noriyoshi CHUBACHI

Faculty of Engineering, Tohoku University,
Aramaki aza Aoba, 980 Sendai Japan

Fracture strength of piezoelectric ceramics is a very important factor in recent miniature size piezoelectric devices and in high-power ultrasonic devices. Although a fracture mechanics testing and designing method should be developed, little progress has been made in the area of applications of piezoelectric ceramics.

This paper describes a strength evaluation of commercially available piezoelectric ceramics, in which the maximum pore size (several ten μm) is greater than grain size (several μm). A parameter of strength evaluation of the ceramics, T_{IC}, is introduced by the fracture mechanics approach as follows; $T_{IC} = K_{IC}/\sqrt{\pi\rho_{pmax}}$, where K_{IC} is fracture toughness and $2\rho_{pmax}$ is the maximum pore size in the ceramic. The T_{IC} is determined as an intrinsic material constant without specimen size effect by the fracture toughness test and SEM observation, and provides a representative fracture strength of the ceramics.

Flexural strength σ_f of various types of piezoelectric ceramic plate has been investigated. A linear relationship $\sigma_f = 0.85T_{IC}$ has been obtained by the experiment for the ceramic plate, in which the thickness d is greater than $50\rho_{pmax}$. A thickness dependence, where σ_f abruptly decreases when the thickness is smaller than $8\rho_{pmax}$, has been reasonably explained by the fracture mechanics approach and represented as; $\sigma_f = (1.77/Y)T_{IC}$, where Y is a function of (ρ_{pmax}/d).

The parameter T_{IC} of strength evaluation of piezoelectric ceramics would be effectively used for the design and material development for piezoelectric devices.

The Dynamic Strength of Piezoelectric Ceramics

R.C. Pohanka
Office of Naval Research Arlington VA 22217
P.L. Smith
Joseph Pasternak
Naval Research Laboratory Washington DC 20375

Progress in understanding the mechanism of dynamic fracture in piezoelectric ceramics is reviewed. The strength of piezoelectric (ferroelectric) polycrystalline materials when measured dynamically has been found to be generally lower than when measured statically. Dynamic strength here refers to strengths measured by driving the specimen electrically at resonance until fracture occurs. Resonant frequencies for the specimens used in this study were in the kilohertz range (typically 15 to 50 KHz). A mechanical fatigue effect has also been observed under these conditions (i.e. a decrease in strength with number of stress cycles). For comparison similar measurements were made of a single crystal of ammonium dihydrogen phosphate (ADP) which is piezoelectric but not ferroelectric. For ADP the static and dynamic strengths were found to be equal. An obvious difference between the polycrystalline ferroelectric and the nonferroelectric single crystal is the existence of domains in the ferroelectric material. These domains give rise to non-linearities in the elastic and dielectric behavior as well as to substantial localized heating at high alternating stresses. A further difference between the single crystal ADP and the polycrystalline ferroelectric was established experimentally, namely that slow crack growth occurrs in the polycrystalline material but not in ADP.

The experimental methods used to measure the static and dynamic strengths, fatigue and defect size will be discussed in detail. Further, a discussion will be included of the extent to which fracture mechanics theory can be used to predict the life of piezoelectric ceramics under dynamic loading conditions.

ANALYSIS OF SOLDERING-INDUCED CRACKING OF $BaTiO_3$ CERAMIC CAPACITORS*

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ABSTRACT

Cracks were found in ceramic capacitors after soldering on hybrid microcircuit boards during fabrication. These were cube-shaped units soldered with Sn-Pb eutectic solder using a reflow process. Cracking was most common at locations where manual rework was performed using a soldering iron, although failures did occur at other locations. These capacitors have been used successfully in established component design.

Samples from an older batch of capacitors which had been successfully soldered were compared with cracked and uncracked capacitors from the problem group. X-ray elemental analysis showed significant differences in chemistries of the barium titanate ($BaTiO_3$) insulators, the capacitor plate elements, and the termination and solder layers. In particular, the older capacitor insulators contained significant bismuth (3.8 weight percent Bi_2O_5), while the newer batch had very little.

Crack initiation sites were found along the outer surfaces originating at the metal/ceramic interface; in many cases crack growth from an initial flaw occurred in discrete steps. No evidence was found for mechanical handling damage causing fractures.

Fractographic evidence indicated that thermal stresses at the metal/ceramic interface were the driving force for crack propagation. These stresses could have originated at several times: during the original manufacture of the capacitors, the reflow board soldering process, or subsequent reworking operations.

Fracture toughness and hardness measurements were made from cracks and impressions, respectively, of a Vickers pyramid diamond. The hardness was similar for both capacitor materials; however, the fracture toughness, or resistance to crack propagation, was 4 times lower in the older bismuth-containing capacitor material. The newer capacitor material should have been mechanically superior. Thus, the material was not the source of cracking, but rather a difference in design application between the old and the new.

Further work has continued to: 1) experimentally evaluate the effect on fracture toughness and slow crack growth of the observed compositional changes in barium titanate; 2) experimentally evaluate the thermal shock resistance of as-manufactured capacitors.

*This work performed at Sandia National Laboratories supported by the U. S. Department of Energy under Contract No. DE-AC04-76DP00789.

2:00 p.m. SESSION 9B: Millimeter Wave Materials
Chairman: H.M. O'Bryan

9B-1 Ferroelectric Materials for Electro-Optic Devices at Millimeter Wavelengths - M.B. Klein, Hughes Research Laboratories, USA

9B-2 Dielectric Waveguide Phase Shifters at 94 GHz Using the Electro-Optic Effect in $LiNbO_3$ - M.B. Klein, Hughes Research Laboratories, USA

9B-3 High Frequency Dielectric Properties of $SrTiO_3$ Glass-Ceramics - S.L. Swartz, W.A. Schulze and L.E. Cross, The Pennsylvania State University and W.N. Lawless, CeramPhysics, Inc., USA

9B-4 Submillimeter-Wave-Range Birefringence Indices and Electric Field-Induced Shifts in Ferroelectric Crystals - P.S. Brody, J.P. Sattler and G.J. Simonis, Harry Diamond Laboratories, USA

9B-5 Dielectric Properties of Ferroelectric Tungsten Bronze $Ba_{2-x}Sr_xK_{1-y}Na_yNb_5O_{15}$ Crystals at RF and Millimeter Wave Frequencies - W.W. Ho, W.F. Hall and R.R. Neurgaonkar, Rockwell Science Center, USA

FERROELECTRIC MATERIALS FOR ELECTRO-OPTIC DEVICES AT MILLIMETER WAVELENGTHS*

by

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Malibu, California 90265
(213) 456-6411

The electro-optic effect in bulk crystals is commonly used in the visible spectral region for modulation, switching and frequency multiplication. There is a need for similar active devices at millimeter wavelengths for radar and communications applications. The most promising class of millimeter-wave electro-optic materials are ferroelectric crystals. The important advantage of ferroelectrics at millimeter wavelengths is that their linear and nonlinear dielectric properties are significantly enhanced over those in the visible, due to contributions from lattice vibrations. As a result, large values of dielectric constant and electro-optic coefficients are expected, although increased losses also occur.

Materials such as $LiNbO_3$ and $LiTaO_3$ have been used for phase shifting and amplitude modulation at millimeter wavelengths [1,2]. The losses in these materials are low, but the electro-optic coefficients have values smaller than those required for most device applications. More promising materials include perovskites such as $BaTiO_3$ [3] and tungsten bronze materials such as $Ba_2NaNb_5O_{15}$ (BNN) and $Sr_xBa_{1-x}Nb_2O_6$ (SBN) [4].

We will consider several specific millimeter-wave electro-optic devices and establish performance criteria and figures of merit in each case. We will then survey candidate ferroelectric materials and compare them using the above criteria for device applications. Finally, we will discuss possible techniques for improving the properties of known materials, especially regarding the reduction of absorption losses.

1. E.A. Vinogradov, N.A. Prisova and G.V. Kozlov, Sov. Phys. Solid State 12, 605 (1970).
2. M.B. Klein, Int. J. Infrared and Millimeter Waves 2, 239 (1981).
3. G.D. Boyd, T.J. Bridges, M.A. Pollack and E.H. Turner, Phys. Rev. Lett. 26, 387 (1971).
4. W. Ho, W.F. Hall, R.R. Neurgaonkar, R.E. DeWames and T.C. Lim, Ferroelectrics 38, 833, (1981).

*Supported in part by the Office of Naval Research under Contract N00014-82-C-0226.

DIELECTRIC WAVEGUIDE PHASE SHIFTERS AT 94 GHz USING THE ELECTRO-OPTIC EFFECT IN $LiNbO_3$*

by

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There is an ongoing need for electrically-controlled phase shifters in the millimeter spectral region for radar and communications applications. Presently available devices using ferrites are slow and have large absorption losses. Bulk semiconductors have also been used for phase shifting [1,2] but the devices are complicated structurally, and drive power requirements can be significant. In our experiments, we have used the electro-optic effect in $LiNbO_3$ [3] to construct phase shifters at a carrier frequency of 94 GHz, with improved performance over earlier results [4]. Our devices have response times which are limited only by circuit conditions, and require very little drive power. Furthermore, the use of dielectric waveguide geometry leads to a compact device with few structural components.

In earlier measurements of microwave electro-optic coefficients [3,5], the sample was either mounted in free space or in conventional metal waveguide. Free space mounting requires large samples to minimize diffraction loss, while mounting in conventional waveguide introduces several dimensional tolerances and requires a feedthrough for modulating voltages. If instead the electro-optic material is prepared in the form of dielectric waveguide, then the requirement for large samples or critical dimensional tolerances is removed, and compatibility with other integrated circuit components is facilitated.

In our presentation, we will first discuss the characteristics of H-guide, the dielectric waveguide structure we have chosen for our experiments. We will then describe the design, construction and performance of two phase shifters which differ in their means of coupling from hollow rectangular waveguide to the $LiNbO_3$ H-guide. We will also discuss other millimeter wave control devices which can be implemented using the electro-optic effect in $LiNbO_3$.

1. B.J. Levin and G.G. Weidner, RCA Review 34, 489 (1973).
2. H. Jacobs and M. Chrepta, IEEE Trans. Microwave Theory Tech. MTT-22, 411 (1974).
3. M.B. Klein, Int. J. Infrared and Millimeter Waves 2, 239 (1981).
4. M.B. Klein, Int. J. Infrared and Millimeter Waves 3, 587 (1982).
5. G.D. Boyd, T.J. Bridges, M.A. Pollack and E.H. Turner, Phys. Rev. Lett. 26, 387 (1971).

*Supported in part by Subcontract #62-471915 with California Institute of Technology under Prime Contract N00014-79-C-0839 with the Office of Naval Research.

High Frequency Dielectric Properties of $SrTiO_3$ Glass-Ceramics

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Abstract

Strontium titanate glass-ceramics, prepared by crystallization of strontium titanate-aluminosilicate glasses, are being investigated for possible application as low-loss dielectric materials at microwave and millimeter wave frequencies. Under suitable crystallization conditions, these glass-ceramics exhibit temperature compensated dielectric permittivity, a consequence of the balance between the negative temperature coefficient of the $SrTiO_3$ crystalline phase and the positive temperature coefficient of the residual aluminosilicate glass phase.

Three glass compositions in the $SrTiO_3$-Al_2O_3-SiO_2 system were selected, each with 70-75% by weight of $SrTiO_3$, and variations such that the effects of silica/alumina weight ratio and zirconia nucleation could be determined. Crystallizations were carried out on small glass dics, by heating in a microprocessor controlled furnace at a rate of 100°C/hour to a crystallization temperature in the range of 800-900°C for a soak time of 1 or 10 hours, followed by cooling at 100°C/hour. Dielectric permittivity and loss at several frequencies between 10 KHz and 4 MHz were measured pseudo-continuously with a computer automated system on cooling over the temperature range of 150 to -160°C. High frequency (1 MHz - 1 GHz) permittivity and loss were also measured, and samples have been submitted for analysis at millimeter frequencies.

Submillimeter-Wave-Range Birefringence Indices and Electric Field-Induced Shifts in Ferroelectric Crystals

by

Philip S. Brody and Joseph P. Sattler and George J. Simonis

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Harry Diamond Laboratories, Adelphi, MD 20783

Spectra over the range from 3 to 20^{-1} cm were obtained using the techniques of Fourier transform spectroscopy. A black body source with a stepping Michelson interferometer and composite germanium detector operating at 4.2°K was used to obtain the transform input data. Birefringence, optical absorption, and electric field induced changes in birefringence were obtained for $LiTaO_3$, $LiNbO_3$, and a variety of other ferroelectric materials. A preliminary analysis shows that the average room temperature refractive indices of $LiTaO_3$ over this frequency region are $n_o = 6.45$ and $n_e = 6.31$. The same average indices for $LiNbO_3$ were, respectively, $n_o = 6.67$ and $n_e = 5.02$. The field-induced shifts in birefringence (as changes in refractive index) will also be given. The possibility of electrooptic modulators and phase shifters for the submillimeter-wave range utilizing electro-optic phenomena in ferroelectric crystals will be discussed.

DIELECTRIC PROPERTIES OF FERROELECTRIC TUNGSTEN BRONZE $Ba_{2-x}Sr_xK_{1-y}Na_yNb_5O_{15}$ CRYSTALS AT RF AND MILLIMETER WAVE FREQUENCIES

W.W. Ho, W.F. Hall, and R.R. Neurgaonkar

Permittivity and dielectric loss have been measured for a number of single crystal samples of barium strontium potassium sodium niobate (BSKNN) in three frequency ranges: 0-1 MHz, 30-40 GHz, and 90-100 GHz. This work is part of an ongoing study of millimeter wave properties of ferroelectrics with potential applications in active components such as phase shifters, modulators, and switches. BSKNN has been selected as typifying one extreme in the tungsten bronze family, where all 15- and 12-fold coordinated cation sites are occupied. Measurements on these crystals show significantly lower millimeter wave absorption than is found in strontium barium niobate (SBN) crystals grown by the same techniques. The permittivities along the principal crystal axes showed a substantial decrease with increasing frequencies over the range of observations, which may be indicative of a relaxation mechanism occurring in the GHz frequency region.

3:40 p.m. SESSION 10A: Materials (Preparation)
Chairman: L. Toth

10A-1 Growth and Applications of Ferroelectric Tungsten Bronze Family Crystals - R.R. Neurgaonkar, W.K. Cory and J.R. Oliver, Rockwell Science Center,USA

10A-2 The Growth and Properties of a New Alanine and Phosphate Substituted Triglycine Sulphate (ATGSP) Crystal - C.S. Fang, Y. Xi, Z.X. Chen, A.S. Bhalla and L.E. Cross, The Pennsylvania State University, USA

10A-3 Growth and Characterization of Colored and Monodomain Single Crystals of KH_2PO_4-Type Ferroelectrics and Antiferroelectrics - N.S. Dalal, P. Grandinetti and D. Nettar, West Virginia University, USA

10A-4 Synthesis and Dielectric Characterization of Pb-K-Niobate Saw-Single Crystal - P.K. Pandey and U.Stridhar, Texas A&M University, USA

10A-5 Preparation and Electrical Properties of Thin Film of Antimony Sulphur Iodide (SbSI) - P. Ghosh, A.S. Bhalla and L.E. Cross, The Pennsylvania State University, USA

10A-6 Production and Properties of Undoped and Doped Lead Germanate Thin Films - H. Schmitt, R. Karthein, G.Kleer, University of Saarlandes, Federal Republic of Germany

10A-7 Evaluation of Crystals of Lithium Niobate Doped with MgO or TiO_2 for Waveguiding Applications - R.J. Holmes and Y.S. Kim, Bell Laboratories; D. Smyth, Lehigh University; and C.D. Brandle, Jr., Bell Laboratories,USA

10A-8 Some Interesting Properties of Dislocation Free Single Crystals of Pure and Modified $Sr_{0.5}Ba_{0.5}Nb_2O_6$ - S.T. Liu, Honeywell Corporation and A.S. Bhalla, The Pennsylvania State University, USA

10A-9 Oriented Grain Growth from Lead Germanate $Pb_5Ge_3O_{11}$ Glass-S. Shimanuki, S. Hashimoto and K. Inomata, Toshiba Research and Development Center, Japan

GROWTH AND APPLICATIONS OF FERROELECTRIC TUNGSTEN BRONZE FAMILY CRYSTALS

R. R. NEURGAONKAR,* W. K. CORY AND J. R. OLIVER
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ABSTRACT

The tungsten bronze family compositions have been studied for almost two decades and have been found to be very interesting ferroelectric materials for several device applications including pyroelectric, electro-optic, non-linear optics, millimeter wave and surface acoustic waves. This family embraces some 120 or more known compounds with several solid solutions systems, and within this very extensive group, several members have high Curie temperatures, as well as dielectric, piezoelectric, pyroelectric and electro-optic coefficients.

Single crystal growth of several ferroelectric bronze compositions such as $Sr_{1-x}Ba_xNb_2O_6$ (SBN), $Sr_2KNb_5O_{15}$ (SKN), $K_3Li_2Nb_5O_{15}$ (KLN) and $Ba_{2-x}Sr_xK_{1-y} - Na_yNb_5O_{15}$ (BSKNN) have been studied and are discussed in this paper. Tungsten bronze crystals are difficult to grow; and the growth depends strongly on the thermal gradients near the solid-liquid interface, the Curie temperature, and the unit cell dimensions. The results of this study show that smaller unit cell bronzes, e.g., SBN and SKN, have cylindrical growth habits with 24 well defined facets while the larger unit cell bronzes grow in square shape with 4 well-defined facets.

Low frequency dielectric, piezoelectric and electro-mechanical coupling coefficients have been evaluated for many of these tungsten bronze crystals. Significant changes in the dielectric and piezoelectric properties can be obtained with changes in composition, and significant differences in the physical properties, e.g., k_{33}, d_{33} and d_{15}, can be observed between the large and small unit cell bronzes. The data show SBN and BSKNN to be very promising for many electro-optic, pyroelectric and SAW device applications.

THE GROWTH AND PROPERTIES OF A NEW ALANINE AND PHOSPHATE SUBSTITUTED TRIGLYCINE SULPHATE (ATGSP) CRYSTAL

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ABSTRACT

A modified alanine doped triglycine sulphate (ATGS) crystal has been grown with partial substitution of H_2SO_4 with H_3PO_4. Growth of the ATGSP crystal from a unipolar ATGS seed in the temperature range 30-40°C gives a unipolar bulk crystal with lower permittivity ($\varepsilon_r \sim 30$) and higher pyroelectric coefficient ($6.5 \cdot 10^{-4}$ c/k.m^2) than pure TGS. In the doping range used, the higher pyroelectric coefficient is traced to a significantly larger spontaneous polarization P_s ($\sim$5 μc/cm^2 at room temperature). Tangent δ is below 0.01 over the whole frequency range from 100 Hz to 100 KHz.

GROWTH AND CHARACTERIZATION OF COLORED AND MONODOMAIN SINGLE CRYSTALS OF KH_2PO_4-TYPE OF FERROELECTRICS AND ANTIFERROELECTRICS

N. S. Dalal, P. Grandinetti and D. Nettar
Department of Chemistry, West Virginia University, Morgantown, WV 26506

With a view to obtaining selectivity in non-linear optical absorption and harmonic generation, we have grown optical quality crystals of KH_2PO_4-type ferroelectrics and $NH_4H_2PO_4$-type antiferroelectrics with colors ranging from blue to orange by suitable impurity doping and/or UV/γ-irradiation. The color centers have been identified by magnetic resonance and optical spectroscopy. The dielectric relaxation and phase transition properties of the doped crystals do not differ significantly from those of undoped samples. It has also been possible to grow crystals with a predominantly monodomain character, which can be further enhanced via temperature cycling through the Curie points of the samples. While the exact mechanism of this (monodomain) behavior is not yet understood, the effect has been found to be quite a useful aid in the spectroscopic characterization, since it results in a significantly enhanced (spectra) resolution. The presentation will focus on the techniques of growth of crystals with specific colors, monodomaining, spectral characterization, and relevance to possible applications in non-linear optics and laser technology.

SYNTHESIS AND DIELECTRIC CHARACTERIZATION OF Pb-K-NIOBATE SAW-SINGLE CRYSTAL*

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Lead-potassium-niobate, $Pb_2KNb_5O_{15}$ (PKN), is a member of the tungsten-bronze family of the type $A_6B_{10}O_{30}$, where A represents Ba, Pb, Sr, Ca, Na, K, etc.; and B represents Nb or Ta. PKN is both ferroelectric and ferroelastic and it can be considered as a pseudo-binary compound represented by $2PbNb_2O_6 \cdot KNbO_3$. Its piezoelectric and electromechanical properties make it a leading material for the fabrication of temperature compensated surface-acoustic-wave (SAW) devices. Details of the two new methods for the growth of PKN single crystals will be discussed. A specific charge composition has been developed with high purity grade K_2CO_3, PbO, and Nb_2O_5 chemicals which is used to synthesize these crystals by the flux growth technique between 1200 and 900°C. Several fluxes such as $PbO \cdot B_2O_3$, $PbO \cdot P_2O_5$, $PbO \cdot V_2O_5$, K_2CO_3, etc., have also been tried and a variety of crystal sizes and morphologies have been obtained with the different fluxes employed. Crack free large crystals of PKN have been grown by the top-seeded method using excess of PbO and K_2CO_3 in the charge. X-ray diffraction studies of our crystals indicate that they belong to the c-centered orthorhombic class. The values of the lattice constants are consistent with those reported for this material in various publications. Optical inspection reveals both 90° and 180° domains. The real part of dielectric constant shows an anomaly at 469°C. Electrical conductivity shows two anomalies at 476°C and 496°C which are attributed to a ferroelectric and ferroelastic transition, respectively.

Thermal behavior of the dielectric constant, conductivity and polarization of these crystals (PKN) between room temperature and 600°C will be presented and compared with the literature values.

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*Work Supported by Air Force Office of Scientific Research: Grant #AFOSR-82-0312.

PREPARATION AND ELECTRICAL PROPERTIES OF THIN FILM OF ANTIMONY SULPHUR IODIDE (SbSI)

by

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Antimony sulphur iodide (SbSI) is a member of a most interesting family of a ferroelectric semiconductors with formula $A^{V}B^{VI}C^{VII}$. The transition in the case of SbSI is accompanied by an exceedingly high permittivity, pyroelectricity and piezoelectricity in the ferroelectric region. In the ferroelectric phase SbSI belongs to an orthrhomibic point group mm2 and exhibits a very large structural and growth anisotropy along the polar c-axis. Thus the material is an attractive candidate for fabricating c-axis oriented thin film. In the present paper we report the preparation and electrical properties of the single crystal films prepared by the recrystallization of the glassy SbSI thin films. The films were oriented along the polar c-axis. The present technique eliminates the requirement of the single crystal substrate for the single crystal thin film deposition and hence the c-axis oriented SbSI films can be prepared on a variety of substrates: glass slides coated with electrode materials (e.g., Au, SnO_2, etc.), amorphous substrates, polycrystalline and single crystal silicon.

Production and Properties of Undoped and Doped Lead Germanate Thin Films

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Lead Germanate crystals show sufficient pyroelectric properties for simple applications. But it is shown by some authors, that the room temperature pyroelectric coefficient increases with a definite incorporation of e.g. Ba on the Pb-site or Si on the Ge-site [1] [2]. The increase is mainly caused by the shift of the phase transition temperature to lower values than 177°C. In this way, pyroelectric response properties comparable to those of TGS can be reached.

On the other hand, thin films of pyro- and ferroelectrics are of interest because of their special properties, as for example the possibility to produce in a simple relatively cheap way large area samples. Therefore, thin films of doped and undoped Lead Germanate $Pb_5Ge_3O_{11}$ were produced by sputtering. The production process is shortly reported. The pyroelectric and ferroelectric properties of thin films of the pure Germanate as well as of doped materials are presented. The results and future aspects are discussed.

[1] R. Watton, C. Smith, G.R. Jones, Ferroelectrics 14, 719-721, (1976)

[2] W. Eysel, R.W. Wolfe, R.E. Newnham, J. Amer. Ceram. Soc. 56, 185-188, (1973)

Evaluation of Crystals of Lithium Niobate Doped With MgO or TiO_2 for Waveguiding Applications

BY

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Abstract

Crystals of lithium niobate doped with MgO or TiO_2 were investigated for their potential as substrates in various waveguiding applications. A study was made of the diffusion of titanium into these crystals as a function of Li/Nb ratio and temperature. Results are compared to those obtained from undoped crystals. Crystals of the desired Li/Nb ratio were obtained by vapor phase equilibration (VPE) in two phase mixtures of $LiNbO_3$ and Li_3NbO_4 to provide a source of Li_2O or $LiNb_3O_8$ to provide a sink of Li_2O. The course of the VPE reaction was followed by a sensitive thermogravimetric analysis system. The composition of the crystals was determined by TGA and verified by Curie temperature measurements. Diffusion of Ti into the doped crystals was studied by electron probe micro-analysis. The diffusivity of Ti (D_{Ti}) in congruent $LiNbO_3$ doped with 10.9 mole % MgO is 4.9×10^{-12} cm^2/sec at 1050°C. This is about five times the value in undoped $LiNbO_3$ at the same temperature. The diffusivity of Ti in congruent $LiNbO_3$ doped with 2.9 mole % TiO_2 is 1.9×10^{-12} cm^2/sec at 1050°C, or nearly twice the value in undoped $LiNbO_3$. From the data, information was obtained about the nature and concentration of ionic defects in the doped $LiNbO_3$ crystals. Mechanisms for Ti incorporation into these materials are postulated.

Some Interesting Properties of Dislocation Free Single Crystals of Pure and Modified $Sr_{0.5}Ba_{0.5}Nb_2O_6$

by

S.T. Liu[1] and A.S. Bhalla[2]

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High quality dislocation free single crystals of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN) and rare earths doped SBN are gorwn for infrared pyroelectric detector and electro-optic applications. Pyroelectric and dielectric properties on these crystals are measured over a temperature range from liquid nitrogen to 150°C. The dislocation free crystals have higher pyroelectric coefficients and retain the total pyroelectricity in successive heating cycles through the phase transition. Electro-optic measurements are also made on these crystals. Both pyroelectric and electro-optic coefficients increase with an increase in rare earth doping concentration in SBN crystals. Pyroelectric coefficients lie in the range from 400 to 2500 $\mu C/m^2K$ and linear electro-optic r_{33} coefficients increase from 2.3 to $7x10^{-10}$ cm/V. The relationship between pyroelectric and electro-optic coefficient (r_{33}) is examined and discussed.

ORIENTED GRAIN GROWTH FROM LEAD GERMANATE $Pb_5Ge_3O_{11}$ GLASS

S.Shimanuki, S.Hashimoto and K.Inomata

Toshiba Research and Development Center,
Toshiba Corporation, Kawasaki 210, Japan

The composition of lead germanate, $Pb_5Ge_3O_{11}$, which is known to be a ferroelectric with a Curie temperature near 177°C in the crystalline phase, has a large pyroelectric coeffient suitable for infrared detetors.(1) Since sigle crystals of $Pb_5Ge_3O_{11}$ grown by the Czochralski method are too fragile to be cut and often obtain many micocracks when cut or polished, other techniques for preparing large thin single crystals with the c-planes are required for sensitive infrared detectors.

In the present work, oriented grain growth from glassy $Pb_5Ge_3O_{11}$ was studied by the glass-recrystallization technique without melting. $Pb_5Ge_3O_{11}$ can be readily prepared in the glassy state by rapid quenching from the melt. Thin plates of glassy $Pb_5Ge_3O_{11}$ about 0.1 mm to 1 mm thick were prepared from the melt using the twin roller apparatus and so on. These glassy thin plates were isothermally recrystallized at 600°C to 700°C for 15 minutes to 24 hours.

Glassy plates more than 0.5 mm thick were almost cracked during heating at the temperature near 500°C owing to the phase change, for less than 0.4 mm thick but not cracked at all. In glassy plates less than 0.2 mm thick, anomalous grain growth easily occured when heated at the temperature near 0.95Tm, where Tm is the melting temperature of $Pb_5Ge_3O_{11}$, and many large hexagonal grains up to 2 mm in cross-section were grown from glassy plates. Their large grain were oriented with the c-plane parallel to the plate surfaces, which was confirmed by X-ray diffraction pattern

(1) G.R.Jones, N.Shaw and A.W.Verre, Electronics Letters, 8, 345(1972). K.Takahashi, I.M.Hardy, R.E.Newnham and L.E.Cross, in Proceedings of the 2nd Meeting on Ferroelectric Materials and Applications (1979), pp257-262.

3:40 p.m. SESSION 10B: Piezoelectrics (General)
Chairman: H. Frederikse

10B-1 *Piezoelectricity and Inhomogeneith in Ceramics*, Polymers and Bone (invited) - Wendell Williams, University of Illinois, USA

10B-2 Rare-Earth Substituted Piezoelectric $PbTiO_3$ Ceramics for Acoustic Wave Applications (invited) - H. Takeuchi, Hitachi Research, Japan

10B-3 Structural Studies of Mn Stabilized Lead Zirconate Titanate - Y.S. Ng and S.M. Alexander, Plessey, Australia

10B-4 Preparation, Properties and Applications of Thin Ferroelectric Films of PLZT - H. Volz and K. Koger, Standard Elektrik Lorenz and H. Schmitt, University of Saarlandes, Federal Republic of Germany

10B-5 R.F. Magnetron Sputtering of Ferroelectric PZT Films- S.B. Krupanidhi, N. Maffei and M. Sayer, Queen's University, Canada

10B-6 The Use of Guided Acoustic Interface Waves in the Study of Differentially Poled Piezoelectric Ceramics - H.A.Kunkel and B. A. Auld, Stanford University, USA

10B-7 PVF_2 Bimorphs as Active Elements in Wind Generators, V.H. Schmidt, M. Klakken and H. Darejeh, Montana State University, USA

Piezoelectricity and Inhomogeneity in Ceramics, Polymers and Bone (invited) Wendell Williams, University of Illinois, USA

(No abstract)

Rare-earth Substituted Piezoelectric $PbTiO_3$ Ceramics for Acoustic Wave Applications

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Piezoelectric and acoustic wave properties of $PbTiO_3$ ceramics modified by partial substitution of rare-earths for the Pb, particularly $(Pb, Ln)(Ti, Mn)O_3$ (Ln = La, Pr, Nd, Sm, Eu, or Gd) ceramics, are extensively investigated. It is found that Nd substitution dramatically decreases the temperature coefficient of surface acoustic wave delay time. A zero temperature coefficient can be achieved in the $(Pb, Nd)(Ti, In, Mn)O_3$ system with appropriate compositions. Furthermore, it is possible to reduce the temperature coefficient of resonance frequencies for various bulk wave modes to zero by changing the combination of Nd and In concentrations. Surface acoustic wave filters and bulk wave resonators with high temperature stability are fabricated using these ceramics. It is also found that $(Pb, Sm)(Ti, Mn)O_3$ ceramics have exceptionally large electromechanical anisotropy (ratio of electromechanical coupling factor for thickness vibration to that for planar vibration is above 15). Extensive studies of the resonant properties of rectangular strip resonators make it clear that Sm substituted ceramics would be very useful in high frequency array transducer applications. A 7.5MHz linear array ultrasonic probe employing these ceramics is developed for medical use. Some examples of 7.5MHz imaging offer much better resolution than 3.5MHz imaging using PZT probes.

STRUCTURAL STUDIES OF Mn STABILISED LEAD ZIRCONATE TITANATE

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ABSTRACT

Piezoelectric compositions Pb $(Mn_u Nb_v Ni_w Ti_x Zr_y) O_3$ where $u + v + w + x + y = 1.0$ were studied by means of X-ray powder diffraction, Scanning electron microscopy and thermal analytical techniques. The assumed B site substitutions of Mn, Nb and Ni for Ti or Zr have important consequences on the electric-acoustic behaviour of the lead zirconate titanate compositions; with Mn in particular possessing dominating influence on the stability at high stress applications. This paper reports the structural changes as the levels of Mn, Nb and Ni were varied and proposes the possible reaction mechanism involved.

Preparation, Properties and Applications of thin Ferroelectric films of PLZT

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PLZT (lead-lanthanum-zirconate-titanate) films are prepared by rf diode sputtering from a target, eight inches in diameter, manufactured by hot-pressing of ceramic powder. The parameters of the process are of great influence on film composition. Gas pressure, substrate bias, power and PbO excess of the target are important. Substrate temperatures above 500 °C during the process are necessary to get perovskite structure which is a precondition for ferroelectric behaviour.
The structure was determined by XRD. The ferroelectric behaviour was examined by measuring of polarisation versus voltage and permittivity and loss versus temperature;after treatment of the films is not necessary.
With the field parallel to the surface of the film a permittivity of 2500 was measured, comparable to ceramic value, whereas with the field perpendicular the dielectric constant was only 500. A polarisation of 50 µ Cb/cm is produced by an applied field of 600 kV/cm.
The capacity versus temperature plot shows two anomalies which are also observed at PLZT ceramic material.
The dielectric loss versus temperature behaviour is different to the ceramic. This might be caused by the different thermal expansion coefficients of substrate and film.

R.F. MAGNETRON SPUTTERING OF FERROELECTRIC PZT FILMS

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CANADA

The large electromechanical coupling coefficient and dielectric constant of PZT ceramics have commended them for the fabrication of acoustic transducers for the generation of bulk and surface waves. Efforts are being made towards the deposition of acoustic quality PZT thin films with a view of utilizing them as substrates for thin film SAW transducers.

Thin films of PZT have been deposited by R.F. magnetron sputtering method using Ar and Oxygen as sputtering media and targets prepared under different conditions. The growth conditions were varied as a function of oxygen partial pressure (0 - 100%), sputtering pressure, rate of gas flow, substrate temperature, nature of substrates and post-deposition annealing. Films of thicknesses 1.0 - 4.0 microns were deposited for different studies and the rate of deposition accounted was about 200 Å/min. The uniformity of films appears to be governed by sputtering pressure and erosion area of the targets.

PZT films have been characterized in terms of crystallinity (X-ray diffraction), stoichiometry (Electron microprobe analysis) and surface morphology (SEM). The films are highly resistive and transparent. The room temperature dielectric constant was in the range of 500 - 700 and the conductivity varied between 10^{-8} - 10^{-10} $ohm^{-1}cm^{-1}$. We report the ferroelectric behaviour in terms of dielectric constant, d.c. conductivity and polarization reversal as a function of temperature.

The feasibility of utilizing these PZT films in SAW device applications, in comparison with well established materials like ZnO, is being examined by considering the respective piezoelectric parameters.

THE USE OF GUIDED ACOUSTIC INTERFACE WAVES IN THE STUDY OF DIFFERENTIALLY POLED PIEZOELECTRIC CERAMICS

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Transition zones between regions of opposite polarization in differentially poled piezoelectric ceramics (analogous to domain walls in single crystals) have been demonstrated as suitable waveguide structures for the propagation of acoustic interface waves.[1] Since the acoustic wave is ducted along the transition zone, it will have a strongly cumulative interaction with the zone and hence will be very sensitive to small changes in zone structure and material properties. For this reason, we have employed these guided interface waves in a comparative study of a variety of commercially available piezoelectric ceramics. Ceramic disks are differentially poled using partial electrodes which cover half of each disk. Acoustic waves are launched into the resulting transition zone by means of a small edge-bonded transducer affixed to the disk edge. Pulse velocity measurements are reported and used to characterize each ceramic sample. A heterodyne laser probe capable of detecting surface vibrations on the order of 10^{-2} Å is used to measure the transverse vibration profile of the acoustic wave as it travels along the interface. In addition, the transverse spatial variation of remnant polarization through the transition zone is measured by means of a standard pyroelectric laser scan technique,[2] and this polarization profile is compared to the corresponding vibration profile for each ceramic. Conclusions are drawn regarding the characteristics of these interface waves relative to various material properties.

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[1] H.A. Kunkel and B.A. Auld, Proc. 1981 IEEE Ultrasonics Symposium, 438-443, IEEE Cat. No. 81CH1689-9.

[2] A. Hadni, J.M. Bassia, X. Gerbaux, and R. Thomas, Appl. Opt., 15, 2150-2158 (1976).

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PVF_2 BIMORPHS AS ACTIVE ELEMENTS IN WIND GENERATORS*

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Abstract - The application to wind electric generation of bimorphs constructed of two sheets glued back-to-back of the piezoelectric polymer poly(vinylidene fluoride), or PVF_2, is discussed. First, some fundamentals of piezoelectric behavior and of cantilever beam oscillations are reviewed. Then test results are presented for electrically driven PVF_2 bimorphs oscillating in air and in vacuum, from which damping factors are derived. Next, two particular vertical axis wind generator designs are described employing such oscillating cantilever bimorphs which are forced into oscillation by the alternating direction of the wind forces acting on them during each rotor revolution. One design consists of a Savonius rotor with S-shaped cross-section, the center part of the blade being a PVF_2 bimorph and the blade tips being made of aluminum foil with C-shaped cross section. The other design has two cantilever-mounted bimorph blades extending in the circumferential direction, with their tips tied together by a nylon line to provide the necessary centripetal force at high rotation speed. Wind tunnel test results for both designs are presented. Finally, economic factors are discussed together with the effect of possible improved polymer properties on generator output.

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